The Molecular Configuration of Diphenyl Ether as Revealed by Dipole Moment Data.

By Keniti HIGASI and Shojiro UYEO.

(Received February 18, 1939.)

The dipole moments of 2,2′-dinitro-, 2,2′-diiodo- and 2,2′-dimethyl-diphenyl ethers were measured in benzene and hexane solutions at 27° and 50°. Four isomers of dimethyl-diphenyl ethers were also studied in benzene solution at 30°. The results obtained for them lead to the conclusion that each benzene ring is perpendicular to the other ring in the molecules considered.

It is not long ago that diphenyl ether, quite a familiar substance to chemists, was found to be playing an important role in the natural world, its skeleton being often found in extracts from plants etc. For instance the work of H. Kondo and his pupils[1] might be mentioned, who discovered the skeleton of this molecule in many alkaloids extracted from plants proper to Japan. In connection with this, Y. Asahina and his co-workers[2] showed that diphenyl ether is also the mother structure of some acids which are found in lichens. Moreover, certain alkaloids, derivatives of diphenyl ether, have recently been found to be of special interest from the chemotherapeutical point of view.[3] Thus, it has become necessary for pharmaceutists as well as for chemists to make a research into the molecular configuration of diphenyl ether.

Many investigations of this substance are known from the side of pure physics and chemistry and many heated discussions have taken place about the valency angle of its oxygen atom. The paper of Hare and Mack[4] is probably the first one relating to this angle. It was based on the collision area method, and gave the angle as 107°, but this value is not certain. We must mention next, the investigation by the dipole moment method, by which an abnormally large angle was deduced at first.[5] But the interpretations of the results were severely criticized by Bennett,[6] who concluded the angle of 109.5° as the more trustworthy. Afterwards, the problem of the valency angle was reexamined by Sutton and Hampson[7] and the angle of diphenyl ether was determined as 128°±4°.[8]

---

(1) Kondo and Tomita, *Arch. Pharm.*, **274** (1936), 65.

(2) Asahina and co-workers, *Ber.*, **66** (1933), 689, 893, 1031, 1215, etc.; see also Richter-Anschutz, "Chemie der Kohlenstoffverbindungen," Vol. II, 1, 394-398.

(3) Unpublished.

(4) Hare and Mack, *J. Am. Chem. Soc.*, **54** (1932), 4272.

(5) Hampson, Farmer, and Sutton, *Proc. Roy. Soc.* (London), A, **143** (1933), 147; Bergmann and Tschudnowsky, *Z. physik. Chem.*, B, **17** (1932), 107; Smyth and Walls, *J. Am. Chem. Soc.*, **54** (1932), 3230.

(6) Bennett, *Trans. Faraday Soc.*, **30** (1934), 853.

(7) Sutton and Hampson, *ibid.*, **31** (1935), 945.

(8) Quite recently a revision of this angle was carried out by Coop and Sutton, by making a new determination of dipole moment in the vapour phase, *J. Chem. Soc.*, **1938**, 1869. The corrected value is 124°±5° which shows a better agreement with the value of Maxwell than their earlier one.

On the other hand, using the electron diffraction method, Maxwell and his co-workers[9] obtained the value of 118°±3°, which lies between 128° and 109° (Fig. 1).

Contrary to the valency angle of oxygen, little attention has been paid to the problem of the structure of the molecule as a whole, i.e. about the orientation of each benzene nucleus in it. This is in sharp contrast to the development of study on the stereo-chemistry of diphenyl derivatives. Pauling,[10] however, suggested in conversation with Sutton that the two benzene rings might be fixed in the same plane—a result which is expected if there be strong resonance among the following structures A and B (Fig. 2). But there seemed no further support for it than the apparent widening of the angle of oxygen.[7] The other structure which the organic chemists imagine instinctively to

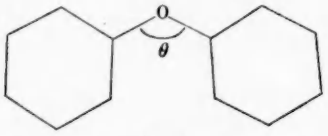
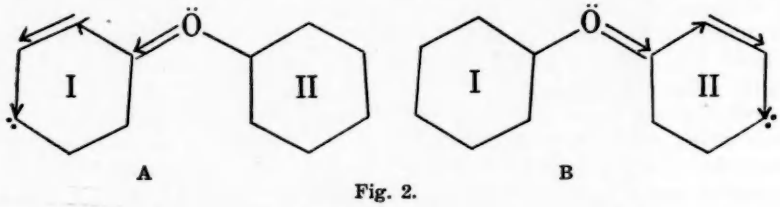


Fig. 1.



A B

Fig. 2.

be stable is that the two benzene rings are perpendicular to the plane of the valency of oxygen. For instance, Smyth[11] seemed to hold this opinion when he spoke of the rotational vibration around this position.

Morino[12] has recently made calculations on the interaction force between the H atoms of the neighbouring rings. One of the results is that the plane structure corresponds to a big increase in the potential energy and is unstable unless a pronounced resonance does occur. The second result is that Smyth's structure does not correspond to the lowest position of this potential energy, and that this condition is attained when one benzene ring is approximately perpendicular to the other (Fig. 3). The present investigation was undertaken in order to examine the suggestions of Pauling and Smyth in view of the recent research of Morino.

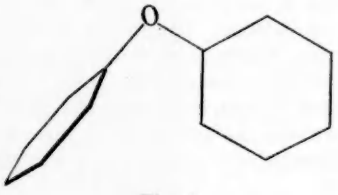


Fig. 3.

Experimental.

In order to realise the aim thus outlined, it was decided to measure dipole moments in solution and to do this over a wide range of temperature

(9) Maxwell, Hendricks, and Mosley, *J. Chem. Phys.*, **3** (1935), 699.
(10) Cited in the paper of Sutton and Hampson, *Trans. Faraday Soc.*, **31** (1935), 945.
(11) Smyth and Walls, *J. Am. Chem. Soc.*, **54** (1932), 3230.
(12) Private communication; the details of his calculation will appear shortly.

with the use of as many solvents as possible. Attention had also to be given to the choice of the solute substances; and 2,2′-dinitro- and 2,2′-diiodo-diphenyl ethers (m.p. 115° and 66° respectively) were prepared[13] in the present research, the reason being that these substances can be obtained in the form of pure crystals and also because they have many advantages over their position isomers in the discussion of molecular structure. Five isomers of dimethyl-diphenyl ethers, the pure samples of which had been prepared by Dr. Tomita[14] and were kindly given to us, were also studied for comparison.

Full details of the present research, i.e. the apparatus, the data of dielectric constants and densities, preparations of materials and their purity etc. will not be described here, because they may be found in other places.[15] In the following tables the results are summarized in six columns: (1) The sample employed as solute, (2) the temperature in °C., (3) the solvent employed, (4) the polarisation, (5) the dipole moment calculated from $P - MR_D$, (6) the dipole moment calculated after Groves-Sugden,[16] viz. $P - 1.05\,MR_D$.

The results of these tables present many features. One is the small solvent effect as seen from the difference between the apparent moments in solution. This gives a clear proof that the observed moments are fairly trustworthy and moreover, that benzene does not exert such an anomalous solvent action to the solute as it does on ethylene chloride.[17] From this, one can safely expect that the small temperature coefficient of moment in benzene is reliable. Moreover, one may notice that the difference between μ and μ' is quite small in the case of dinitro- and diiodo-compounds. There-

Table 1.

Substance	t°C.	Solvent	P (c c)	μ (D)	μ′ (D)
2,2′-Dimethyl-diphenyl ether	27	Benzene	75.2	0.83	0.73
	50	,,	74.4	0.84	0.73
	27	Hexane	74.7	0.82	0.72
2,2′-Dinitro-diphenyl ether	27	Benzene	970	6.64	6.62
	50	,,	890	6.57	6.56
	27	Dioxan[18]	992	6.72	6.70
2,2′-Diiodo-diphenyl ether	27	Benzene	230	2.72	2.69
	50	,,	225	2.78	2.74
	27	Hexane	228	2.70	2.67

(13) Higasi and Uyeo, *J. Chem. Soc. Japan*, **60** (1939), 204.

(14) Tomita, *J. Pharm. Soc. Japan*, **57** (1937), 76.

(15) Apparatus, Higasi, this Bulletin, **13** (1938), 158. The data of dielectric constants and densities, Uyeo and Higasi, *J. Chem. Soc. Japan*, **60** (1939), 199, 204. Preparation of Materials, Higasi and Uyeo[13], Tomita[14].

(16) Groves and Sugden, *J. Chem. Soc.*, **1935**, 971.

(17) Mizushima, Morino, and Higasi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **25** (1934), 159.

(18) 2,2′-Dinitro-diphenyl ether is hardly soluble in hexane, so dioxan was employed as solvent instead of hexane. As this solvent may not be so neutral as hexane, allowance must be made of its specific action on the moment.

Table 2.

Substance	t°C.	Solvent	P(c.c)	μ(D)	μ'(D)
3,3′-Dimethyl-diphenyl ether	30	Benzene	101.0	1.40	1.35
4,4′-Dimethyl-diphenyl ether[19]	,,	,,	104.6	1.46	1.41
3,4′-Dimethyl-diphenyl ether	,,	,,	102.0	1.42	1.36
3,4-Dimethyl-diphenyl ether	,,	,,	109.0	1.53	1.49

fore, it is evident that the error arising from atomic polarisation is insignificant in these molecules. For dimethyl-diphenyl ethers, however, this error becomes rather serious on account of their small moments.

It may be concluded, therefore, that the moments of the above molecules are not much affected by solvent,[20] temperature, and also by the choice of atomic polarisation, and if dimethyl-diphenyl ethers should be regarded as an exception, these are affected only by the last.

Discussion.

For convenience' sake we shall first discuss the results of Table 1. And then, using the conclusions drawn from them, we shall discuss the dipole moments of isomeric dimethyl-diphenyl ethers (Table 2).

Free Rotation and Contour Map of Moment. The molecule of 2,2′-disubstituted diphenyl ether has four polar linkages, i.e. two C–O bonds and two C–X bonds (X being the substituent), but we may represent the two C–O bond moments by its resultant (μ_1) which bisects the valency angle of the oxygen atom (Fig. 4). According to the classical view of organic chemistry, this molecule has two axes of rotation, so that for describing the intramolecular configuration, two parameters, θ_1 and θ_2 are necessary which will be defined as follows.

Consider a Cartesian co-ordinate system (Fig. 5) and let the Z axis coincide with the direction of μ_1 and choose the YZ plane on the C–O–C plane. Now, each substituent is capable of rotation around the corresponding C–O line, the azimuths of rotation θ_1 and θ_2 for μ_2, right and left respectively, will be defined as follows: θ_1 and θ_2 are zero, when they lie on the YZ plane on the right side of the corresponding C–O line, and the positive sense is taken as in the left hand screw (see Fig. 5).

(19) The result for 4,4′-dimethyl-diphenyl ether may be compared with that of Hampson, Farmer, and Sutton, *Proc. Roy. Soc.* (London), A, **143** (1933), 147. They gave it $P = 104.5$ c.c. at 25°C. which corresponds to $P = 103.8$ c.c. at 30°C. The dipole moment of this substance was newly determined in the vapour phase by Coop and Sutton, *J. Chem. Soc.*, **1938**, 1869. The result was $\mu = 1.44$ D, and P_2 at 30° estimated from it is 108.0 c.c.

(20) It may be too bold to say so without any corresponding data in the vapour phase. But according to the theory of solvent effect, this error would not be serious—not so serious at least as 4,4′-disubstituted diphenyl ether.

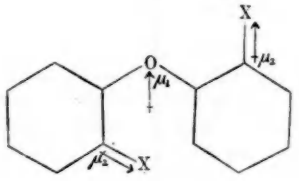


Fig. 4.

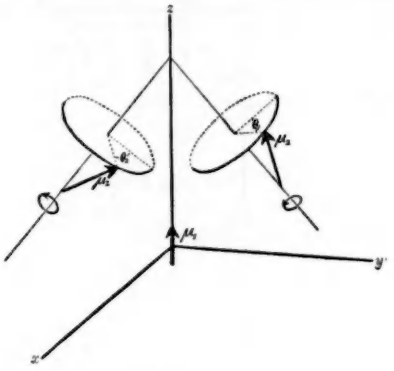


Fig. 5.

And the moment of a molecule as a whole, μ can be expressed by the following relation.

$$\mu = (\mu_x^2+\mu_y^2+\mu_z^2)^{\frac{1}{2}} \tag{1}$$

where

$$\left.\begin{aligned} \mu_x &= \mu_2(\sin\theta_1+\sin\theta_2)\sin 60^\circ \\ \mu_y &= \mu_2(\cos\theta_1+\cos\theta_2)\sin 60^\circ\cos\varphi \\ \mu_z &= \mu_1+2\mu_2\cos\varphi\cos 60^\circ+\mu_2\sin\varphi(\cos\theta_1-\cos\theta_2)\sin 60^\circ \end{aligned}\right\} \tag{2}$$

where φ denotes half of the valency angle of oxygen.

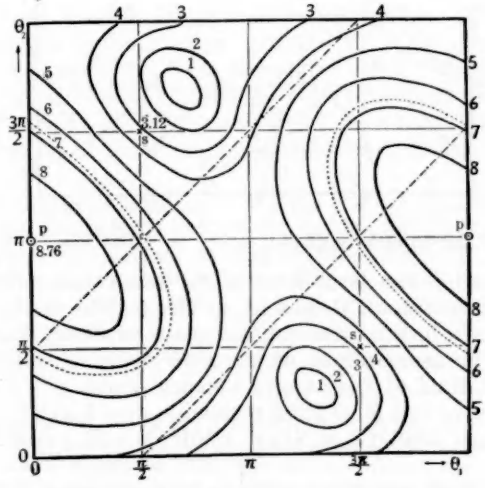


Fig. 6. 2,2′-Dinitro-diphenyl ether: $\mu_1 = 1.14$D, $\mu_2 = 3.80$D.

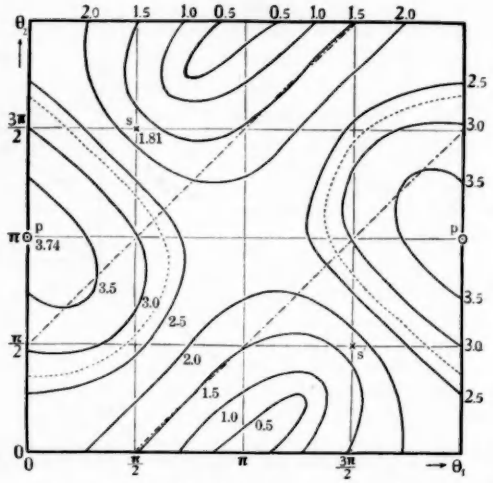


Fig. 7. 2,2′-Diiodo-diphenyl ether: $\mu_1 = 1.14$D, $\mu_2 = 1.30$D.

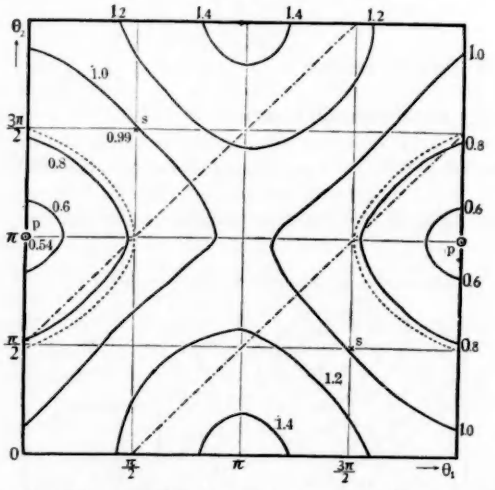


Fig. 8. 2,2′-Dimethyl-diphenyl ether: $\mu_1 = 1.14$D, $\mu_2 = -0.30$D.

As μ_1, μ_2 and φ can be estimated, we can easily calculate the total moment μ as a function of θ_1 and θ_2. The results of the calculation by this way are shown in the three contour maps of dipole moment (see Fig. 6, 7, and 8). The assumptions which were made in this calculation are as follows. (1) Half of the oxygen valency angle, $\varphi = 118°/2$; (2) the resultant moment of two C−O bond moments, $\mu_1 = 1.14$D;[21] (3) the C−X bond moment, $\mu_2 = 3.80$D(X = NO_2), 1.30D(X = I), −0.30D(X = CH_3).

(21) According to the new determination by Coop and Sutton, *J. Chem. Soc.*, **1938**, 1869, the moment of diphenyl ether in the vapour phase is 1.14D.

It is clear that the reliability of the contour maps (Fig. 6, 7, and 8) is dependent upon the validity of these assumptions as well as that of the above equations. Therefore, we shall discuss these more carefully afterwards. But in the following, we shall assume that the contour maps are fairly correct, and using them we shall discuss the molecular configuration of diphenyl ether.

The Plane Formula of Pauling. There are three plane formulae for disubstituted diphenyl ether, i.e., A, B, and C (Fig. 9). In the case of 2,2′-disubstituted compounds, however, the structures B and C should be excluded on account of big repulsion.

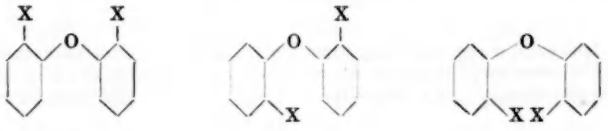


Fig. 9.

No explanation will be needed for the structure C. On constructing a model[22] of a 2,2′-disubstituted molecule, it will be also understood why the structure B is untenable. For instance, at a model of 2,2′-diiodo-diphenyl ether, one would find the distance between I and H atoms (of the neighbouring ring), if they are in the structure B, much smaller than the H–I distance of the chemically combined atoms. For dinitro-diphenyl ether the N–H distance for B would be estimated as 0.3 Å in contrast to the N–H distance of 1.0 Å of the combined atoms. Therefore, it is quite evident that a considerable repulsion occurs at this structure.[23]

Thus the only possible structure is A which corresponds to a point, $\theta_1 = 0$, $\theta_2 = \pi$ in the contour maps (marked by ⊙ in Fig. 6, 7, 8). And the moments at this position are calculated as 8.76D, 3.74D, 0.54D for dinitro-, diiodo-, and dimethyl-diphenyl ethers, respectively, while the observed moments are 6.64D, 2.72D, and 0.83D, respectively. The differences are certainly too large to be explained as experimental errors.

The Configuration according to Smyth. If we neglect the mutual interaction between the substituent groups, according to Smyth, there should be two probable configurations of disubstituted diphenyl ether; i.e. trans (D) and cis (E) forms (see Fig. 10) and the molecule might be supposed to be vibrating near both positions. In the 2,2′-disubstituted compounds, however, the substituents X approach each other and a big repulsion results at the cis position. For example, in 2,2′-diiodo-diphenyl ether the

(22) A molecular model can be easily constructed with the use of data found in books like Stuart, "Molekülstruktur," Sidgwick, "Covalent Links in Chemistry." See also Pauling and Huggins, *Z. Krist.*, **84** (1933), 205.

(23) In order to make this structure stable, the valency angle of oxygen should be widened to a great extent, more than ca.160°.

I–I distance becomes 2Å for the E structure, while that of the combined atoms is 2.7Å. In the molecule of 2,2′-dinitro-diphenyl ether, the O–O

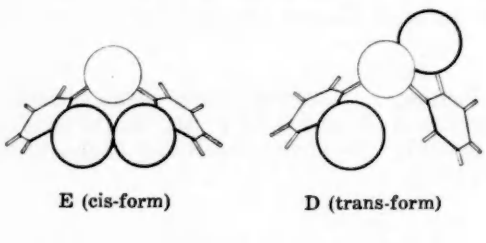


Fig. 10. Molecular model according to Smyth of 2,2′-disubstituted diphenyl ether.
○ Oxygen atom. ● Substituent.

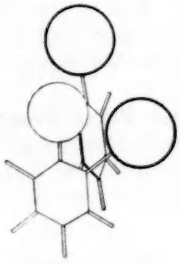


Fig. 11. Molecular model according to Morino of 2,2′-disubstituted diphenyl ether.

distance for E becomes less than 1.9Å, which is certainly larger than that of the combined atoms 1.2Å, but smaller than that of closest packing 2.72Å. Therefore this position seems to be also improbable.

As a conclusion from the above, we may say that the trans form D has a much lower potential energy than cis form E and it will be sufficient to consider vibrations near this position which corresponds to the points $\theta_1 = \frac{\pi}{2}$, $\theta_2 = \frac{3\pi}{2}$ and $\theta_1 = \frac{3\pi}{2}$, $\theta_2 = \frac{\pi}{2}$ (marked with × in the contour diagrams).

If the vibration has a small amplitude, we may expect at inspection of the map that the moment will not differ very much from that for the structure D. Therefore, for 2,2′-dinitro-, diiodo-, and dimethyl-diphenyl ether, the moments of 3.1D, 1.8D and 1.0D are estimated respectively. The difference between these and the observed moments are much more pronounced.

The Molecular Configuration according to Morino. The potential due to the repulsion between H atoms of the neighbouring rings was carefully traced by Morino of the Chemical Institute and it was found that the lowest valley in the potential diagram lies on two straight lines $\theta_2 = \theta_1 \pm \frac{\pi}{2}$ in the contour map—approximately speaking, one benzene ring is situated perpendicular to the other.

If all the positions on these lines are equally probable, the mean moment $\bar{\mu}$ is calculated as follows by putting $\theta_2 = \theta_1 \pm \frac{\pi}{2}$ in equation (1).

$$\bar{\mu}^2 = \frac{\int_0^{2\pi} \mu^2 d\theta_1}{\int_0^{2\pi} d\theta_1} \qquad (3)$$

This definite integral is easily evaluated, and the resultant equation is

$$\bar{\mu}^2 = (\mu_1 + \mu_2 \cos\varphi)^2 + 1.5\mu_2^2 \qquad (4)$$

Putting $\varphi = 59°$, $\mu_1 = 1.14$D, $\mu_2 = 3.80$D, 1.30D, −0.30D for $-NO_2$, −I, $-CH_3$ respectively, the following values shown in the third column of the table are obtained.

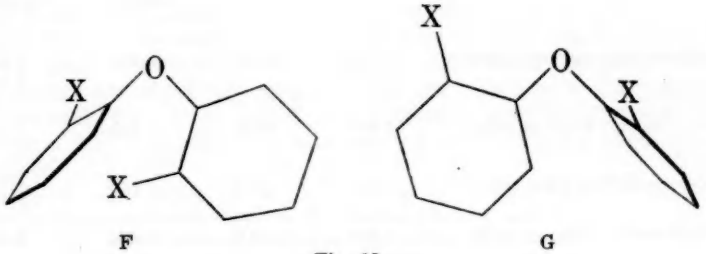
Table 3.

Substance	Observed value	Calculated moment		
		Morino	Pauling	Smyth
2,2′−$(NO_2C_6H_4)_2O$	6.64D	5.59D	8.76D	3.1D
2,2′−$(IC_6H_4)_2O$	2.72D	2.41D	3.74D	1.8D
2,2′−$(CH_3C_6H_4)_2O$	0.83D	1.05D	0.54D	1.0D

Although, the calculated moments do not show close agreement with the experimental values, the differences between them are not so marked as in the cases of the Pauling and Smyth structures.

In the above calculation we assumed that any position on the lines of $\theta_2 = \theta_1 \pm \frac{\pi}{2}$ is equally probable.[24] But this assumption becomes certainly invalid when a big atom or group is introduced to the 2,2′-position. For instance, the structure F would be rather improbable on account of great repulsion (Fig. 12). The dipole moment at this position, $\theta_1 = \pi$, $\theta_2 = \frac{3\pi}{2}$ $\left(\theta_2 = \theta_1 + \frac{\pi}{2}\right)$, $\theta_1 = \pi$, $\theta_2 = \frac{\pi}{2}\left(\theta_2 = \theta_1 - \frac{\pi}{2}\right)$ is much smaller than the average value, viz. 3.72D, 1.52D for dinitro- and diiodo-diphenyl ether, while it is larger than the average value in the case of dimethyl-diphenyl ether, i.e. 1.25D.

Therefore, if this structure is excluded in the above calculation the resulting moments would approach the observed values. Therefore, we may consider as follows: each benzene ring can rotate around the corresponding C–O axis on the two conditions: (1) one ring is almost perpendicular to the other and (2) the rotation near the position F is not allowed.



F G

Fig. 12.

(24) This condition is satisfied in the case of diphenyl ether, but not necessarily so in the case of its derivatives.

In the contour map of dipole moment, we denoted the positions which correspond to the observed moment by the dotted lines (····) and the $\theta_2 = \theta_1 \pm \frac{\pi}{2}$ relation by (—·—·—) lines. It should be noted that the crossing of two dotted lines is always found near the positions $\theta_1 = \frac{\pi}{2}$, $\theta_2 = \pi$ or $\theta_1 = \frac{3\pi}{2}$, $\theta_2 = \pi$ in each map for the three substances. This is an interesting fact which should not be overlooked as a mere coincidence. The simplest explanation for it is, of course, to suppose that the molecule considered has the solid structure G (Fig. 12) corresponding to the position $\theta_1 = \pm\frac{\pi}{2}$, $\theta_2 = \pi$. (See also the model in Fig. 11.)

Alternatively, we may assume rotational vibration near this position. Because any vibration near it, (if its amplitude be small), would not much alter the value of average moment from that at G. Moreover, this vibrational structure explains the small temperature coefficient of dipole moment, because the increase in amplitude which should accompany the rise of temperature will not exert a very marked influence on the average dipole moment which is easily understood from the nature of the contour map.

The Dipole Moments of Dimethyl-diphenyl Ethers. So far, we have considered, 2,2′-disubstituted compounds only. Next, we shall discuss the results of the other derivatives of diphenyl ether in a few words. We can treat them just as we did before, and in the following table we show the comparison of the observed and calculated values (as the error due to the atomic polarisation is most serious in them, both μ and μ' are tabulated).

The observed moments show fairly good agreement with the mean moments calculated according to Morino. In this calculation, we assumed any position satisfying $\theta_2 = \theta_1 \pm \frac{\pi}{2}$ is equally probable. This as-

Table 4.

	Observed moment		Calculated moment	
	μ	μ'	Morino	Pauling[25]
3,3′-Dimethyl-diphenyl ether	1.40D	1.35D	1.35D	0.76D 1.33D 1.84D
3,4′-Dimethyl-diphenyl ether	1 42D	1.36D	1.40D	1.12D 1.68D
3,4-Dimethyl-diphenyl ether	1.53D	1.49D	1.46D	1.27D 1.48D
4,4′-Dimethyl-diphenyl ether	1.46D	1.41D	1.45D	1.46D

(25) The following values are assumed in this calculation:

$\theta = 125°$, $\mu_1 = 1.14$D, $\mu_2 = -0.35$D

sumption can be justified in these cases because the substituents are separated far from the neighbouring benzene rings and also from each other, i.e. the repulsion force is expected to be small.

From the same reason, there are a few possible plane structures deduced from Pauling's theory which differ in dipole moment, and the observed moments lie between the corresponding maximum and minimum values.[25] But this is insignificant, because the Pauling structure was found to be rather contradicting in the above case of 2,2′-disubstituted diphenyl ether.

Notes on Assumptions. (1) *The valency angle of oxygen.* In the above discussion the valency angle of oxygen was assumed to be 118°.[9] What becomes if the angle be different from the assumed value, will be the next problem to be solved. If the widening of the angle did occur, Pauling's structure might be right after all? In order to answer this question, the following table may be found helpful in which the values of bond moments which are needed for Pauling's and Smyth's structure are given for different values of the valency angle.

Table 5.[26]

Valency angle of oxygen	$\mu(C-NO_2)$		$\mu(C-I)$	
	Pauling	Smyth	Pauling	Smyth
90°	3.16	7.79	0.90	2.24
100°	2.92	8.56	0.83	2.46
110°	2.78	9.58	0.79	2.76
120°	2.74	11.00	0.78	3.16
130°	2.78	13.00	0.79	3.74
140°	2.92	16.10	0.83	4.62
150°	3.16	21.22	0.90	6.10

The bond moments assumed in the present paper are as follows: $\mu(C-NO_2) = 3.80$, $\mu(C-I) = 1.30$, $\mu(Ph_2O) = 1.14$. The same value for $\mu(Ph_2O)$ is employed in the calculation of Table 5.

At a glance at the above table it is evident that Smyth's structure can be ruled out, because it corresponds to a too big bond moment even when the angle decreases to 90°. On the other hand the bond moments for Pauling's structure are smaller than the value ordinarily proposed. With the widening of the angle, this difference gets smaller indeed, but even at $\theta = 150°$ it is still of a magnitude for which some explanation[27] is required.

(26) The moments are expressed in Debye units, i.e. 10^{-18} e.s.u.

(27) The interaction moments which account for this will be

$$\delta\mu(C-NO_2) = 0.64D \qquad \delta\mu(C-I) = 0.48D.$$

And if we take the moments of nitrobenzene and iodobenzene in the vapour phase, 4.23D and ca. 1.6D as the standard, $\delta\mu(C-NO_2)$, $\delta\mu(C-I)$ will be 1.07D and 0.7D respectively. (Continued to the next page.)

(2) *Induction effect.* In the above discussion we neglected entirely the induction effect in the first approximation. But this effect on the bond moments of the molecule can be easily estimated[29] and in the following table the results of estimation are shown.

Table 6.[26] Induction effect on bond moment.

Substance	Calculated moment without correction of induction	Calculated moment with correction of induction effect
2,2′-$(NO_2\cdot C_6H_4)_2O$	8.74	8.49
2,2′-$(I\cdot C_6H_4)_2O$	3.74	3.05
2,2′-$(CH_3\cdot C_6H_4)_2O$	0.54	0.54

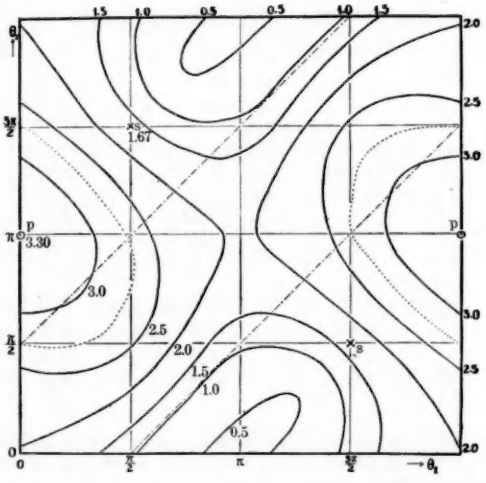


Fig. 13. 2,2′-Diiodo-diphenyl ether: $\mu_1 = 1.10$D, $\mu_2 = 1.10$D.

It should be emphasized that the induction effect in 2,2′-dinitro-diphenyl ether is too small to be considered. Therefore if the change of bond moment be needed for this molecule it is clear that induction effect

On the other hand, we must recall that the group moment $\mu(C-X)$ was assumed to lie on the C—X line in eq. (2). This assumption is certainly valid, when no interaction of moment occurs. But if such an interaction as considered by Sutton, *Trans. Faraday Soc.*, **31** (1935), 945, occurs, we must employ $\sin(60°+\delta)$, $\cos(60°+\delta)$ instead of $\sin 60°$, etc. in the above equations. And if we confine our attention to the plane formula, the change in the angle of oxygen will bring about the same result as the introduction of δ, viz., the widening of the angle can be interpreted as the finite value of δ.

Therefore the writers do not regard this as a comp'ete proof that the plane structure is improbable.

alone[28] cannot account for it. In the molecule of 2,2′-diiodo-diphenyl ether, however, a rather significant effect is expected from the big polarizability of iodine atom. Therefore a contour diagram of this molecule was constructed with the use of $\varphi = 59°$, $\mu_1 = 1.10$D, $\mu_2 = 1.10$D instead of $\mu_2 = 1.30$D (Fig. 13). The comparison of it with Fig. 7 shows that almost the same conclusions can be drawn from here too.

(3) *Further test of bond moment.* In the following table the values of the bond moments assumed in the present paper are compared with those of Smallwood and Herzfeld[29] and also with the moments of C_6H_5X.[30]

Table 7.[26]

Bond	Bond moment assumed value μ_2	4,4′-$(X \cdot C_6H_4)_2O$		Bond moment Smallwood[29]	$\mu(C_6H_5X)$[30]
		Calc. with μ_2	Observed		
C—NO_2	3.80	2.78	2.79(10) 2.62(7)	3.75	3.98(B) 4.23(G)
C—I	1.30	0.55	—	1.25	1.38(B)
C—CH_3	0.30	1.45	1.46	0.43	0.37(G)

Determinations in gas phase, and in benzene solution are indicated by G and B, respectively.

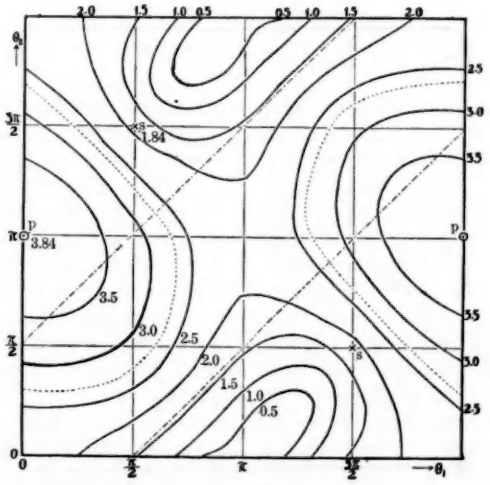


Fig. 14. 2,2′-Diiodo-diphenyl ether: $\mu_1 = 1.14$D, $\mu_2 = 1.35$D.

(28) The interaction effect besides induction arises from "resonance" or "electromerism," and it seems fair not to disregard this. But it seems rather difficult to treat this effect quantitatively, except making some arbitrary allowance for it. This allowance was introduced to a certain extent, indeed, in the consideration of the various contour maps. (Fig. 13, 14, 15, and 16. See also foot-note 27.) The effect of "resonance" on the vector additivity of bond moment is often very important in aromatic compounds. "Other effect" of disubstituted benzene should be reexamined on this ground. We intend to treat this problem quantitatively in a near future, and there we shall discuss the topic of the present paper again.

(29) Smallwood and Herzfeld, *J. Am. Chem. Soc.*, **52** (1930), 1919.

(30) A Table of Dipole Moments, Appendix, *Trans. Faraday Soc.*, **30** (1934).

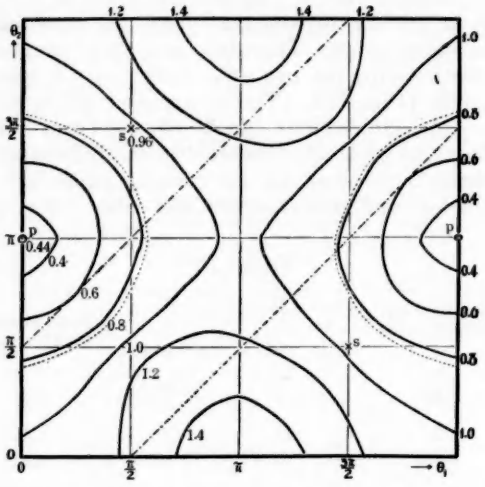


Fig. 15. 2,2′-Dimethyl-diphenyl ether: $\mu_1 = 1.14$D, $\mu_2 = -0.35$D.

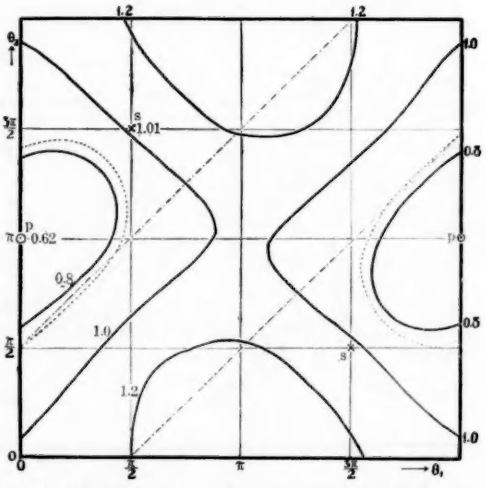


Fig. 16. 2,2′-Dimethyl-diphenyl ether: $\mu_1 = 1.14$D, $\mu_2 = -0.26$D.

The values of the present paper are near those employed by Smallwood and Herzfeld. In the middle column of the same table the moments of 4,4′-$(X{\cdot}C_6H_4)_2O$ are shown. The calculated values were obtained with the use of the bond moments in the present paper. It should be noticed that they are in good agreement with the observed moments.

A further examination of this problem was made by drawing the contour maps with the choice of other bond moments (Fig. 14, 15, and

16). It is certain from this that the change in bond moment so far as it is small, does not alter the essential conclusions reached in the above discussion.

In conclusion the writers wish to thank Professor E. Ochiai and Professor S. Mizushima for many valuable suggestions in connection with the present investigation. They are also indebted to Dr. Tomita for the gift of materials, and to Dr. Morino for kind discussions.

The Institute of Physical and Chemical Research, Tokyo and Pharmaceutical Institute, Faculty of Medicine, Imperial University of Tokyo.

Extended Co-ordination Theory. I. Configuration of Simple Compounds of Typical Elements.

By Ryutaro TSUCHIDA.

(Received March 2, 1939.)

The present paper is to deal with an extension of Werner's co-ordination theory to simple compounds.

Chemical valences are usually classified into electrovalence, covalence and co-ordinate covalence, but it is impossible to draw sharp boundary-lines among them. It is a question of degree than of nature. We can easily understand this fact from the following examples of metallic halides. Whereas stannic chloride forms molecules of the formula $SnCl_4$, chromic chloride is a multinuclear complex[1] in which each chromic ion is surrounded by six chlorine ions octahedrally[2] and each chlorine ion is attached to three chromic ions by co-ordinate covalences. In solid cobaltous chloride, the covalent nature is less remarkable, though its crystal structure[3] shows that it is also a multinuclear complex. Even among bivalent cations we can find covalent compounds such as mercuric chloride which is one of the typical compounds having molecules. The colour of silver bromide is due to the second absorption band,[4] i.e., the co-ordination band, because neither silver nor bromine ion has the first absorption band.[5] The colour of silver iodide is also attributed to the co-ordination band from the same reason, and it is of interest to note that each silver ion is surrounded by four iodine ions tetrahedrally[6] just as in the yellow

(1) R. Tsuchida, this Bulletin, **13** (1938), 436; *J. Chem. Soc. Japan*, **59** (1938), 586.
(2) N. Wooster, *Z. Krist.*, **74** (1930), 363.
(3) H. Grime and J. A. Santos, *Z. Krist.*, **88** (1934), 136.
(4) R. Tsuchida, this Bulletin, **13** (1938), 388; *J. Chem. Soc. Japan*, **59** (1938), 819.
(5) R. Tsuchida, *J. Chem. Soc. Japan*, **59** (1938), 731.
(6) R. B. Wilsey, *Phil. Mag.*, **46** (1923), 487.

complex ion $[HgI_4]^-$ which has only the second and the third band.[5] In short, solid silver bromide and iodide are not built up purely by electrovalence, but partly by co-ordinate covalence. Sodium chloride is usually regarded as one of the typical ionic compounds, but spectroscopic consideration reveals that it has tendency, though slight, of co-ordination.[1] As can be seen from these examples, it is impossible to distinguish the kinds of valences. For the purpose of the unitary treatment, therefore, every chemical valence may be regarded as a co-ordinate covalence or its extreme case. Thus by assuming that ions and molecules are built up by co-ordinating ions, molecules and electrons around cations, configuration of all the simple as well as complex compounds may be easily found.

The co-ordination is a mutual saturation of co-ordination numbers on both sides of the donor and the acceptor. For example, in $[Cu(NH_3)_4]^{++}$, both the co-ordination numbers of copper and nitrogen are satisfied by co-ordinating NH_3 around Cu^{++}. Any ion in a compound may, therefore, be taken as the center of co-ordination in discussing the configuration of the compound. For the sake of convenience and consistency, however, cations as given by Kossel[7] are chosen as the co-ordination center. Thus in methane quadrivalent carbon cation is taken as the center and four hydrogen anions as ligands. In ammonia three hydrogen anions and a pair of electrons are assumed to co-ordinate around quinquevalent nitrogen cation. The valency of nitrogen, recovering two electrons, is now three. But in ammonium chloride, quinquevalent nitrogen cation is surrounded by four hydrogen anions and the resulting charge of the complex ion is plus one, the valency of nitrogen remaining unchanged.

The typical element, i.e., the element belonging to the subgroup A of the periodic table, is assumed to ionize forming the cation of the charge corresponding to the number of the group. Then the electronic configuration of the cations of the typical elements are as shown in Table 1.

Table 1.

Group	I	II	III	IV	V	VI	VII	Electron distribution of the ion										The lowest co-ordination function
Charge	+1	+2	+3	+4	+5	+6	+7	1 s	2 s	2 p	3 s	3 p	3 d	4 s	4 p	4 d	4 f	5 s	5 p	5 d	5 f	6 s	6 p	
Ions	Li	Be	B	C	N	O	F	2																2s
	Na	Mg	Al	Si	P	S	Cl	2	2	6														3s
	K	Ca						2	2	6	2	6												4s
			Ga	Ge	As	Se	Br	2	2	6	2	6	10											4s
	Rb	Sr						2	2	6	2	6	10	2	6									5s
			In	Sn	Sb	Te	I	2	2	6	2	6	10	2	6	10								5s
	Cs	Ba						2	2	6	2	6	10	2	6	10		2	6					6s
			Tl	Pb	Bi	Po	—	2	2	6	2	6	10	2	6	10	14	2	6	10				6s
	—	Ra						2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	7s

(7) W. Kossel, *Ann. Physik*, [4], **49** (1916), 229; *Z. Elektrochem.*, **26** (1920), 314.

These cations are co-ordinated with anions and pairs of electrons. Let us now consider the configuration of methane for example. In this compound four hydrogen anions are assumed to co-ordinate around the central quadrivalent carbon cation. All the ligands of a co-ordination compound are co-ordinated so that they may be equally distributed in space. Applying this rule in the present case, the four hydrogen anions should equally divide the space around the central carbon cation. There are two such ways, i.e., the tetragonal and the tetrahedral configuration. Now it is necessary to decide which configuration is more suitable. Let us imagine the electron distribution after co-ordination of the four hydrogen ions, by which four pairs of electrons are introduced. We may expect that these pairs of electrons should be distributed symmetrically by the above mentioned rule and at the same time should satisfy the wave-functions for the carbon ion. Now four functions, 2s, $2p_X$, $2p_Y$ and $2p_Z$, are taken, and then we may expect to find that the symmetry of the resultant electron density distribution is either tetragonal or tetrahedral. The electron density distribution for 2p's together gives an octahedral symmetry, whereas that for 2s a spherical symmetry. The resultant symmetry is, therefore, octahedral. Thus it is easily seen that the tetrahedral configuration completely fits the symmetry. Four hydrogen anions are, therefore, co-ordinated tetrahedrally around the carbon ion, the resulting molecule being similar to that derived by Pauling[8] by the ingenious method of hybridization. In ammonia three hydrogen anions and a pair of electrons are co-ordinated around a quinquevalent nitrogen cation. It is postulated that a pair of electrons has approximately the same share as other anions. Thus the co-ordination number is also four as in methane, and the configuration of ammonia is pyramidal, the angle $\angle$ HNH being 109°. For water there are two such pairs of electrons, and from a similar reasoning as above, the configuration is V-shaped, the angle $\angle$ HOH being 109°. In all these examples the co-ordination number was four and four eigenfunctions were taken for co-ordination. Let us define such eigenfunctions as co-ordination functions. The lowest co-ordination functions for cations of typical elements are shown in the last column of Table 1. It is postulated that the co-ordination functions could not be of different principal quantum numbers. Then for all the cations of typical elements, the co-ordination function begins with s, because the postulate forbids the participation of 3d functions in co-ordination with 4s and 4p for K^+ and Ca^{++} and so on. Now we can derive the configurations of the compounds of these ions for various co-ordination numbers.

The general rule for co-ordination stated above allows us only six kinds of co-ordination numbers, i.e., 1, 2, 3, 4, 6 and 8. As can be easily seen, the ions of the elements in the first horizontal series in the periodic table, i.e., Li, Be, B, C, N, O and F, could not co-ordinate more than four ligands, because the L-level contains only four eigenfunctions, 2s and $2p^3$, and the above-stated postulate forbids the participation of 3s and 3p in co-ordination with 2s and 2p. The relation between the co-ordination number and the configuration is shown in Table 2 with examples.

(8) L. Pauling, *J. Am. Chem. Soc.*, **53** (1931), 1367.

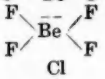
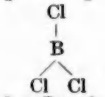
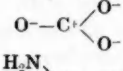
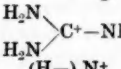
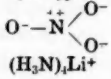
Table 2.

Co-ordination number	Co-ordination functions	Resultant symmetry	Ions and molecules
2	s p	Linear	CO_2, CH_3MgI, BO_2^-, $[FHF]^-$, etc.
3	p p p	Plane-triangular	BCl_3, SO_3, $[C(NH_2)_3]^+$, $CO_3^=$, etc.
4	s p p p	Tetrahedral	CCl_4, $Pb(C_2H_5)_4$, $SO_4^=$, NH_4^+, $[BeF_4]^=$, etc.
6	s p p p d d	Octahedral	SF_6, $[AlF_6]^{3-}$, $[SiF_6]^=$, etc.
8	p p p d d d d d	Hexahedral	$[Ca(C_2H_5OH)_8]^{++}$, etc.

For the co-ordination numbers 3 and 8, the eigenfunction for s is not available as is shown in Table 2, because the participation of the function renders it impossible to find the trigonal and the hexahedral symmetry.

Making use of Table 2, we may easily find the configuration of various ions and molecules without any more consideration than the co-ordination number. Examples are given in Table 3 for the elements in the first horizontal series in the periodic table for which the co-ordination numbers, 1, 2, 3 and 4 only are allowed.

Table 3.

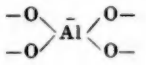
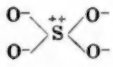
Ion or molecule	Central ion	Ligands	Co-ordination number	Structure	Configuration
$[FHF]^-$	H^+	$2F^-$	2	$F-H^+-F$	Linear
$BeO_2^=$	Be^{++}	$2O^-$	2	$O^- - Be - O^-$	,,
$[BeF_4]^=$	,,	$4F^-$	4		Tetrahedral
BCl_3	B^{3+}	$3Cl^-$	3		Plane-triangular
BO_2^-	,,	$2O^-$	2	$O^- - B^+ - O^-$	Linear
CCl_4	C^{4+}	$4Cl^-$	4	$C(-Cl)_4$	Tetrahedral
$CO_3^=$	,,	$3O^-$	3		Plane-triangular
$[C(NH_2)_3]^+$	,,	$3NH_2^-$	3		Plane-triangular
NH_4^+	N^{5+}	$4H^-$	4	$(H-)_4N^+$	Tetrahedral
NO_3^-	,,	$3O^-$	3		Plane-triangular
$[Li(NH_3)_4]^+$	Li^+	$4NH_3$	4	$(H_3N)_4Li^+$	Tetrahedral

In Table 3 we find $[FHF]^-$, an example of hydrogen bridge. From the present viewpoint, the hydrogen bridge is not so singular as has been usually believed, but one of the special cases of co-ordination. A co-

ordination band[9] due to a hydrogen bridge has been shown in the ultraviolet region. The trigonal configuration of carbonate, nitrate, and guanidonium[10] ions may be easily explained. The complex salts and the simple compounds can be discussed by the same method and their configurations may readily be derived by the same simple consideration. Thus the isomorphism between the sulphates and fluoroborates or orthosilicates and fluoroberyllate may be clearly understood.

The elements of higher atomic number than neon can give ions and molecules of various co-ordination numbers, i.e., 1, 2, 3, 4, 6 and 8. Some of the examples are given in Table 4.

Table 4.

Ion or molecule	Central ion	Ligands	Co-ordination number	Configuration
CH_3MgI	Mg^{++}	CH_3^-, I^-	2	Linear
$[AlF_6]^{3-}$	Al^{3+}	$6F^-$	6	Octahedral
$[AlO_4]^{5-}$	,,	$4O^=$	4	Tetrahedral 
$[SiO_4]^{4-}$	Si^{4+}	$4O^=$	4	,,
SO_3	S^{6+}	$3O^=$	3	Plane-trigonal
SF_6	,,	$6F^-$	6	Octahedral
$SO_4^=$	,,	$4O^=$	4	Tetrahedral 
PO_4^{3-}	P^{5+}	$4O^=$	4	,,
$H_2PO_2^-$	,,	$2H^-$, $2O^=$	4	,,
ClO_4^-	Cl^{7+}	$4O^=$	4	,,

In Table 4 we find sulphur hexafluoride, a compound of "expanded" shell. The octet theory[11] has failed to explain the dodecet structure. The groups SiO_4^{4-} and AlO_4^{5-} are the structural units of various silicate and alumino-silicate minerals.

Anomallies of valence-angles are seen among ions and molecules in which electrons are co-ordinated just as other ligands. For examples in the molecules of ammonia and water, there are pairs of electrons whose spins are neutralized. The present author has devised an automatic method of taking such electrons into consideration, by first removing the electrons from the atom and then co-ordinating them again together with other ligands. This consideration is applicable to all the ions and molecules in which the valencies of the elements of the central cations are lower than the maximum valencies shown by the group numbers in the periodic table. The configuration of such ions and molecules can easily be found automatically without any further consideration by a simple tabular method. Some examples are given in Table 5. In the first column

(9) R. Tsuchida and T. Tsumaki, this Bulletin, **13** (1938), 527.
(10) W. Theilacker, *Z. Krist.*, **76** (1931), 203.
(11) I. Langmuir, *J. Am. Chem. Soc.*, **41** (1919), 252.

is written the ion or molecule whose configuration is required. Then the ligands are tabulated, a pair of electrons and an odd electron being treated just as other ligands. The number of electrons to be co-ordinated can be readily found by balancing the valency of the central ion and the charges of the ligands with that of the entire ion or molecule. Then the co-ordination number is found, which in turn gives the configuration by Table 2.

Table 5.

Ion or molecule	Central ion	Ligands	Co-ordination number	Configuration	Angle		
					Theoretical	Observed	Literature
H_2O	O^{6+}	$2H^-, :, :$	4	V-shaped	109°	105°	
NH_3	N^{5+}	$3H^-, :$	4	Pyramidal	109°	106°	
NO_2^-	,,	$2O^-, :$	3	V-shaped	120°	132°	(12)
NO_2	,,	$2O^-, \cdot$	3	,,	120°	110°–120°	(13)
CO_2	C^{4+}	$2O^=$	2	Linear	180°	180°	
SO_2	S^{6+}	$2O^=, :$	3	V-shaped	120°	122°	(14)
SO_3	,,	$3O^=$	3	Trigonal	120°	120°	(15)
$SO_3^=$	,,	$3O^=, :$	4	Pyramidal	109°	111°	(16)
ClO_2^-	Cl^{7+}	$2O^=, :, :$	4	V-shaped	109°	114°	(17)
ClO_3^-	,,	$3O^=, :$	4	Pyramidal	109°	107°	(18)

The angles derived by this method fairly coincide with the experimental data as can be seen from the table.

As is evident from Tables 2–5, the configuration of a molecule or an ion is determined only by the co-ordination number, if appropriate consideration is given to "non-bonding" electrons.

Summary.

All the chemical linkages may be explained in terms of the co-ordinate covalence. By assuming that molecules and radical ions are built up by co-ordination of molecules, ions and electrons as ligands around central cations whose combining fields are given by sets of wave-functions, the configuration of all the simple as well as complex compounds could be readily found.

Chemistry Department, Faculty of Science,
Imperial University of Osaka.

---

(12) W. H. Zachariasen, *J. Am. Chem. Soc.*, **53** (1931), 2123.
(13) G. Sutherland and W. G. Penny, *Nature*, **136** (1935), 146.
(14) P. C. Cross and L. D. Brockway, *J. Chem. Phys.*, **3** (1935), 821.
(15) H. Gerding and J. Lecomte, *Nature*, **142** (1938), 718.
(16) W. H. Zachariasen and N. E. Buckley, *Phys. Rev.*, **37** (1931), 1295.
(17) G. R. Levi and A. Scherillo, *Z. Krist.*, **76** (1930), 431.
(18) W. H. Zachariasen, *Z. Krist.*, **71** (1929), 517.

On the Nature of Foam. V. Phase Inversion and Foam Formation of Emulsion Consisting of Acetic Acid, Benzene, and Water.

By Tunetaka SASAKI.

(Received March 10, 1939.)

It was reported in the preceding paper[1] that there exist two types of heterogeneous systems of acetic acid – ethyl ether – water (AEW), namely, the system which occasionally produces two types of emulsions (oil-in-water and water-in-oil) according to the two different modes of shaking, and the system which produces only one type of emulsion whatever the mode of shaking. Moreover, it was indicated the existence of a system which can behave both foamy and non foamy according to the two modes of shaking. Present paper describes the influence of the mode of shaking upon the type of emulsion and foam formation of the ternary heterogeneous system of acetic acid–benzene–water (ABW).

Experiments. In ABW-system, acetic acid is soluble in all proportions both in water and benzene, while benzene is insoluble in water. Mutual solubility diagram was obtained in the preceding paper[2] which is showin in Fig. 1. It covers a wide region of heterogeneous system.

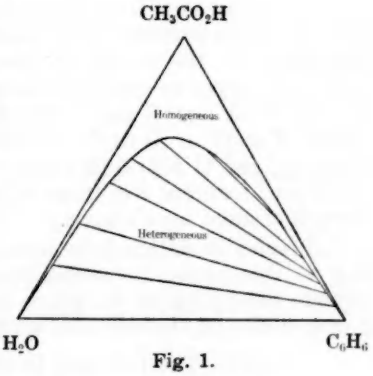


Fig. 1.

A definite volume (10 c.c.) of this heterogeneous system is taken in a test tube and the following two modes of shaking are applied.

(1) The test tube is held by hand vertically, pulled upwards quickly and then brought down slowly. After repeating these motions several times, usual up-and-down shaking is applied.

(2) The upper portion of the test tube is held by hand and the lower portion of it is swung repeatedly. Usual up-and-down shaking is subsequently applied.

The determination of the type of emulsion which is produced by above two modes of shaking is made by observing the process of breaking up of resulting emulsion in the following manner.[1] The emulsion is determined to be O-in-W type[3] when the droplets of disperse phase increase their size as they go upwards and a liquid layer is gradually separated

(1) Sasaki, this Bulletin, **14** (1939). 63.
(2) Sasaki, this Bulletin, **14** (1939), 3.
(3) O-in-Water represents emulsion in which the upper liquid layer of original heterogeneous system is dispersed in the lower one, and W-in-O represents the reverse type to O-in-W.

at the top from the bulk, while it is considered to be W-in-O type[3] when the droplets increase their size as they sink and a liquid layer is gradually separated at the bottom. Thus, in the various heterogeneous systems of ABW, the type of emulsion established by the above two modes of shaking were determined. Some of its data are shown in Table 1.

Table 1.

Composition in volume (c.c.)			Mode of shaking		Composition in volume (c.c.)			Mode of shaking	
Acetic acid	Benzene	Water	(1)	(2)	Acetic acid	Benzene	water	(1)	(2)
50.0	35.0	15.0	O-in-W	W-in-O	22.1	35.9	42.0	O-in-W	O-in-W
45.5	31.8	22.7	O-in-W	W-in-O	21.0	39.1	39.9	O-in-W	W-in-O
41.6	29.2	29.2	O-in-W	W-in-O	20.2	41.5	38.3	O-in-W	W-in-O
38.5	26.9	34.6	O-in-W	O-in-W	19.4	43.8	36.8	W-in-O	W-in-O
36.2	31.2	32.6	O-in-W	O-in-W	18.0	47.8	34.2	W-in-O	W-in-O
33.8	35.8	30.4	O-in-W	W-in-O	16.8	44.6	38.6	W-in-O	W-in-O
32.0	39 1	28.9	O-in-W	W-in-O	15.7	41.8	42.5	O-in-W	W-in-O
30.1	42.8	27.1	W-in-O	W-in-O	15.1	40.1	44.8	O-in-W	W-in-O
28.4	40.3	31.3	W-in-O	W-in-O	14.6	38.9	46.5	O-in-W	W-in-O
26.9	38.2	34.9	O-in-W	W-in-O	14.2	37.8	48.0	O-in-W	W-in-O
25.5	36.2	38.3	O-in-W	O-in-W	13.8	36.8	49.4	O-in-W	O-in-W
23.2	32.8	44.0	O-in-W	O-in-W					

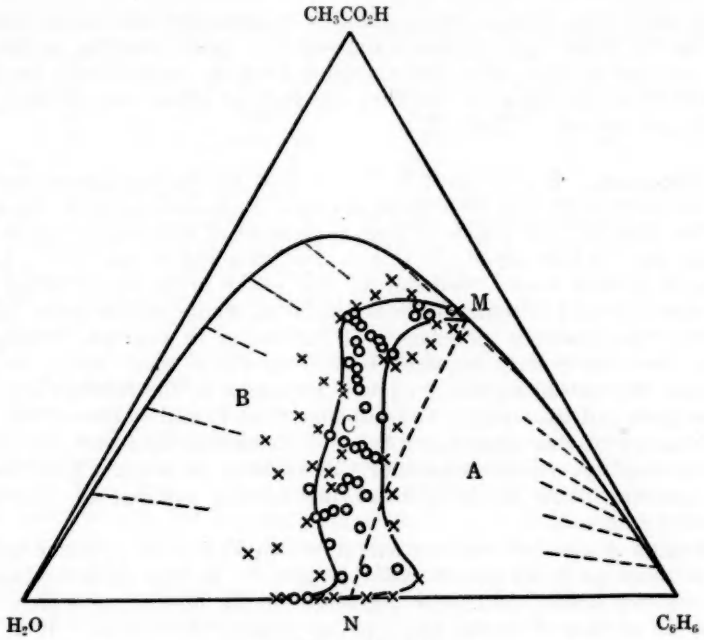
It can be seen from this table that there exist two kinds of systems, that is, those systems which can produce only one type of emulsion independent of the modes of shaking, and those which occasionally produce both types of emulsion according to the different modes of shaking. In Fig. 2, A and B represent the region in which a system simply produces W-in-O or O-in-W emulsion respectively whatever the modes of shaking, and C represents the region in which a system shows the possibility of forming two types of emulsion, namely, it represents the phase inversion zone by shaking.

Precise investigations were further made upon the systems belonging to this phase inversion zone C. A definite volume (10 c.c.) of a system belonging to the phase inversion zone is taken and the following three modes of shaking are applied.

(1) The test tube is shaken as described in (1).
(2) The test tube is shaken as described in (2).
(3) The usual up-and-down shaking alone is applied from the beginning.

The usual up-and-down shaking involved in the above three modes of shaking is performed by the same shaking apparatus and on the same conditions (50 vibrations for 10 seconds with amplitude of 12 cm.) as described in the preceding paper.[4] The type of resulting emulsion is determined by observing the behaviour of breaking up of emulsion, in the same manner as described before. Following quantities were measured

(4) Sasaki, this Bulletin, **13** (1938), 669.



○ phase inversion system.
× O-in-W or W-in-O system.

Fig. 2.

Table 2.

System	Compsition in volume (c.c.)			Mode of shaking			Volume ratio	
	Acetic acid	Benzene	Water	(1)	(2)	(3)	Upper layer	Lower layer
(a)	0.30	5.70	4.00	O-in-W $S_e = 104$ $S_f = 5$ $H = 0.8$	W-in-O $S_e = 26$ $S_f = 0$ $H = 0$	Same as in (2)	1.262	1.000
(b)	0.48	4.52	5.00	O-in-W $S_e = 112$ $S_f = 6$ $H = 0.8$	W-in-O $S_e = 25$ $S_f = 0$ $H = 0$	Same as in (1)	0.905	1.000
(c)	0.48	5.19	4.33	O-in-W $S_e = 130$ $S_f = 6$ $H = 1.0$	W-in-O $S_e = 27$ $S_f = 0$ $H = 0$	Same as in (1) and (2)	1.174	1.000
(d)	4.50	3.00	2.50	O-in-W $S_e = 29$ $S_f = 0$ $H = 0$	W-in-O $S_e = 21$ $S_f = 0$ $H = 0$	Same as in (1)	0.471	1 000

S_e and S_f denote stabilities of emulsion and foam respectively in second, and H represents height of foam in cm.

at the same time, that is, the stabilities of emulsion and foam which are denoted by time required from immediately after shaking to the complete collapse of foam zone and emulsion droplets respectively, the height of foam zone directly after the shaking, and the phase volume ratio. The results are shown in Table 2.

Discussion. It is evident in Fig. 2, that the heterogeneous region of ABW-system is divided into three portions A, B, and C, as in the case of AEW-system.[1] The region A mainly consists of systems having a larger volume of an upper layer (V_u) than that of a lower one (V_l). In such region a system shows tendency of the lower layer being dispersed in the upper one and becomes W-in-O emulsion, whatever the mode of shaking.[1] This tendency increases with difference in volumes between two layers, i.e., the system becomes W-in-O emulsion more easily as it approaches the mutual solubility curve. In region B, the relation is reverse. In the system of this region, V_u is smaller than V_l and so the system shows the tendency of the upper layer being dispersed in the lower one, that is, O-in-W emulsion results whatever the mode of shaking. This tendency also becomes more remarkable as the system approaches the mutual solubility curve.

Region A also involves systems in which V_l is a little larger than V_u, as was observed in the case of AEW-system.[1] In such systems, the lower layer having larger volume is dispersed in the upper one which cannot simply be explained by the above phase volume effect alone. It is rather the case in general that a ternary system shows such anomalies as in this case and in AEW-system.[1] Some other factors must be introduced, in addition to the above volume effect, to explain these phenomena. Specific action of interface was quoted for instance, in the preceding paper.[1]

Phase inversion zone C, namely, the region in which a system shows the tendency of producing both types of emulsion according to the different modes of shaking is situated between two regions A and B as shown in Fig. 2. The mode of shaking described in (1) favours to produce O-in-W emulsion, while the shaking of the mode (2) favours to produce W-in-O emulsion. Recently, the relation between emulsion type and mode of shaking was also indicated by Andreas[5] in the case of a system of immiscible triple layered liquid which is in accordance with our explanations.

The existence of the phase inversion zone was pointed out already in the preceding paper,[1] but the sharp boundary of this zone was not obtained in the case of AEW-system. In the present case, however, this zone is determined distinctly as shown in Fig. 2. The zone C is not situated along the dotted line MN in Fig. 2 which represents the locus of points corresponding to systems of V_u being equal to V_l. This is the case just similar to that of AEW-system. The position of phase inversion zone, therefore, cannot be determined by the volume ratio alone. It is however possible to say that in regions A and B, the effect of relative volume ratio is remarkable, while in phase inversion zone, the effect of modes of shaking as described in (1) and (2) are predominant in de-

(5) Andreas, *J. Chem. Education*, **15** (1938), 523.

termination of emulsion type. The influence of emulsifying agent is absent throughout in this system as in AEW-system.

In Table 2. three systems (a), (b) and (c) were all taken in the phase inversion zone C, so the shaking of the mode (1) or (2) favours to produce O-in-W or W-in-O emulsion respectively in these systems, on the same reason as was explained in the preceding paper.[1] In the present case, intermittent shaking described in (1) is especially effective[6] in producing O-in-W emulsion as it gives time to break relatively unstable W-in-O emulsion droplets produced simultaneously by shaking.

In the case of shaking of the mode (3) where the up-and-down shaking alone is applied from the beginning, these systems show difference in their behaviours. System (a) produces W-in-O emulsion, system (b) O-in-W emulsion and system (c) occasionally produces both types of them.

It was reported in the preceding paper[1] that in the phase inversion zone, those systems which are situated close to the region A show the tendency to produce emulsion of the similar type to that in region A (W-in-O) and those near the region B show the tendency of producing emulsion of the same type as that in region B (O-in-W). These facts were again confirmed in the present experiments. In Table 2, system (a) which is close to the region A, as shown in Fig. 3, has the tendency of producing emulsion of W-in-O type more easily than the other possible type of O-in-W emulsion on shaking. System (b), in the same manner, produces O-in-W emulsion more easily than that of W-in-O type. In the case of system (c), it is distant from both regions A and B, and it has equal tendency of producing both types of emulsions. All these three systems lie on a same tie-line, i.e., they consist of an upper and a lower layers of nearly one and the same composition respectively, and they merely differ in their volume ratio $V_u : V_l$. Above difference in behaviour of emulsion can therefore be ascribed mainly to the effect of volume ratio as shown in Table 2. It must be added that the system (c) which has equal tendencies of establishing both types of emulsions, is not always equally distant from two regions A and B, nor does it coincide with the middle point of a tie-line.

It happens frequently that the type of emulsion once established by a certain mode of shaking cannot be inverted by another mode of shaking, even in the phase inversion system. Thus in the system (b), O-in-W emulsion is relatively stable and simple up-and-down shaking produces emulsion of this type, but once W-in-O emulsion is established by the mode of shaking described in (1), subsequent up-and-down shaking merely favours to produce emulsion of the same type, instead of inverting it to another type. Sometimes, a certain mode of shaking which favours to produce one type of emulsion favours to accelerate the breaking-up of emulsion of another type which otherwise breaks up slowly. W-in-O emulsion of the system (c), for example, requires 130 seconds for the complete separation into two layers when it is left at rest after shaking. The time is reduced to about 84 seconds when it is shaken as described in (2). Such a phenomenon is similar to a demulsifying effect of one type of emulsify-

(6) Briggs, *J. Phys. Chem.*, **24** (1920), 120.

ing agent to emulsion which is stabilized by the emulsifying agent of another type, as indicated by Clowes.[7]

It was suggested in the preceding paper[1] that distinction must be made between the tendency to establish a type of emulsion and its stability, showing the example of AEW-system. The confirmation is further made in the case of ABW-system. It can be seen in Table 2, that the system (a) shows the tendency of producing W-in-O emulsion by the usual up-and-down shaking, although it is far more unstable than O-in-W emulsion.

The general difference in behaviour or appearance between O-in-W and W-in-O emulsions of ABW-system is summarised in Table 3. The

Table 3.

O-in-W emulsion	W-in-O emulsion
Produced by shaking of the mode (1)	Produced by shaking of the mode (2)
Emulsion drops increase their size as they go upwards and a liquid layer is separated upon the bulk. Relatively stable.	Emulsion drops increase their size as they sink and a liquid layer is separated at the bottom. Relatively unstable.
Emulsion is brilliant in light.	Emulsion is frosted and white.
Foamy or non foamy, triple layered foam[2] occurs frequently. Foamy emulsion is nearly silent on shaking.	Non foamy. Emulsion is noisy when shaken.
Air bubbles go upwards quickly with emulsion drops.	Air bubbles go upwards slowly between emulsion props.

nature of ABW-emulsion is somewhat different from that of AEW-emulsion. In ABW-system, O-in-W emulsion is more stable than W-in-O emulsion, while in AEW-system the latter is more stable than the former. It can be observed that heterogeneous system of ABW produces brilliant emulsion drops when O-in-W emulsion is formed on shaking. This is explained from the total refraction caused by emulsion drops which have smaller refractive index than that of dispersing medium. These behaviours can generally be observed in most other heterogeneous systems provided that there exists marked difference in refractive indices between two immiscible components. Emulsion is frosted and white in the case of W-in-O type. Emulsion usually makes noise on shaking, but it turns to be nearly silent when foam, acting as a cushion, is produced. Further, the motion of the air bubbles produced by shaking in the emulsion is also distinctive. In O-in-W emulsion the motion is quick, while in W-in-O emulsion it is slow as if the emulsion is fairly viscous.

Finally, it will be discussed upon the foam formation of ABW-emulsion. System (a), (b) and (c) foams when it is shaken by the mode (1), while it does not foam by shaking of the mode (2), as shown in Table 2. Existence of such a system has already been indicated in the preceding paper[1] for AEW-emulsion and was called foam-nonfoam system. The

(7) Clowes, *J. Phys. Chem.*, **20** (1916), 407.

effect of shaking upon foam-nonfoam system of ABW as described above is, however, just reverse to that of AEW in which foam is produced by shaking of the mode (2), while it is not produced by shaking of the mode (1).

It was concluded in the preceding paper[1] that the region of these foam-nonfoam systems is restricted in a portion of phase inversion zone which at the same time forms a part of foamy region of heterogeneous system. In Fig. 3, foamy region is expressed by B'[2] which is surrounded by a dotted line, and the phase inversion zone is also indicated by C. Hatched portion, therefore, corresponds to foam-nonfoam region of ABW-system. A system of this region foams when it produces O-in-W emulsion,

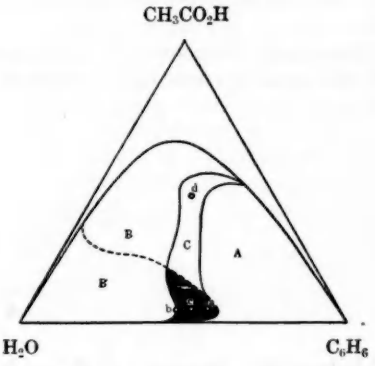
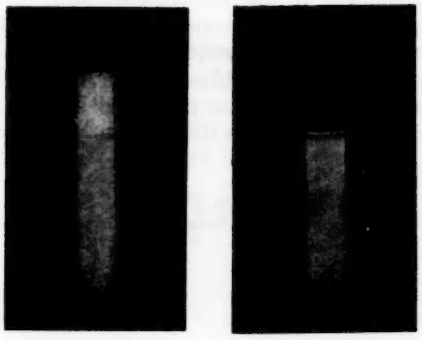


Fig. 3.



Foamy emulsion, produced by shaking of the mode (1).

Non foamy emulsion, produced by shaking of the mode (2).

Fig. 4.

for emulsion droplets having fairly smaller surface tension than the dispersing medium favour to produce triple layered foam.[2] It does not foam when it produces W-in-O emulsion like as the system of A region. Fig. 4 shows an example of such foam-nonfoam system.

The reverse effect of two modes of shakings to the foam formation between ABW- and AEW- systems can be explained by the fact that the foamy region of heterogeneous system is situated in B region (O-in-W region) in the case of ABW-system, while it is situated in A region (W-in-O region) in the case of AEW-system, and so the mode of shaking to produce foamy emulsion is different between two systems.

In the system (d) which is situated in phase inversion zone but not in the foamy region, emulsions of both types can be produced by shaking, but foam is not produced in either of them.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima for his kind guidance. The expense for the experiments has been defrayed from a grant given to Prof. Sameshima by Nippon Gakujutsu Shinkokwai (Japan Society for the Promotion of Scientific Research), to which the author's thanks are due.

Summary.

(1) The heterogeneous region of the system consisting of acetic acid, benzene and water (ABW) is divided into three regions A, B and C, referring to the type of emulsion produced by two different modes of shaking. Systems in region A or B produce water-in-oil or oil-in-water emulsion respectively, whatever the mode of shaking, and those in region C occasionally produce both types of emulsion according to the two modes of shaking. The region C is called the phase inversion zone by shaking.

(2) Some systems of this phase inversion zone behave both foamy and non foamy according to the two different modes of shaking. The existence of such foam-nonfoam system is restricted in a portion of the phase inversion zone which at the same time forms a portion of foamy region of heterogeneous system of ABW.

(3) The difference in nature or behaviour between two possible types of emulsions produced by one and the same system was compared in details, and its discussions were made.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

Chemical Studies by Means of Molecular Beams. VII.* A Method of Measuring the Intensity of Potassium Atomic Beams with an Incandescent Tungsten Surface. Part 1.

By Kumasaburo KODERA.

(Received March 10, 1939.)

Introduction. An incandescent tungsten filament, when placed in alkali metal vapour, emits ions. This is because the atoms of alkali metal which strike the filament are ionized and evaporated. Generally, perfect ionization takes place when the ionization potential of the atoms is considerably smaller than the work function of tungsten.

This phenomenon was first discovered by Langmuir and Kingdon[1] with caesium; and later it was reported by Killian[2] with rubidium and potassium. In the case of sodium and lithium, the ionization can be effected with a tungsten filament whose surface is covered with a monoatomic layer of oxygen.

---

* Preceding papers were published in Japanese in the *J. Chem. Soc. Japan*, **57** (1936), **58** (1937).

(1) I. Langmuir and K. H. Kingdon, *Proc. Roy. Soc.* (London), A, **107** (1925), 61.

(2) T. J. Killian, *Phys. Rev.*, **27** (1926), 578.

In 1929, Taylor[3] applied this phenomenon to the intensity measurement of an atomic beam of alkali metals. A fine tungsten filament surrounded by a cylindrical cathode is placed within the path of an atomic beam. The atoms which strike the filament are ionized and attracted towards the cathode. The ion current thus produced gives the intensity of that part of the atomic beam, provided the ionization is complete. This method of measurement with fine filaments has since been used to advantage but it has a drawback when it is desired to measure the total intensity or a large portion of the intensity of the current at one time. This is especially the case with a weak atomic beam of a large cross section.

This inconvenience may be avoided by using a ribbon of convenient width in place of a fine filament. The way of measurement is quite the same as with a fine filament, except that owing to a considerably larger evolution of heat a suitable additional device around the ribbon is necessary. However, this undesirable heat effect may be reduced to minimum, if we use the method of flashing. The whole cross section of a weak atomic beam is received by an unheated ribbon surface for a certain time, which is then electrically flashed for a short time and the ions thus formed are measured by a ballistic galvanometer.

The present investigation has been carried out with potassium atomic beams to learn the conditions of applicability of this method.

Apparatus. The apparatus used is shown in Fig. 1. F represents an oven for potassium made of nickel chrome steel, the construction being similar to that previously used by Nishibori[4] in our laboratory. The tungsten filaments for heating, which are inserted from the left hand, are not shown in the figure. Potassium atoms gush through the circular orifice O into a highly evacuated space and are caught by the surrounding cooled walls except for those which pass through the second circular orifice Sl and advance as a beam. S at the left side of Sl is a shutter for the atomic beam to which is attached a piece of iron to be operated from outside by a small electromagnet. The movement of the shutter is accurately controlled with a stop-watch electrically connected with it. A copper tube T_1 is cooled by liquid air contained in L_1 and serves to catch all atoms which have failed to pass through Sl. The diameter of O is 0.1 mm. and that of Sl 1.7 mm. The detector chamber is shown on the right

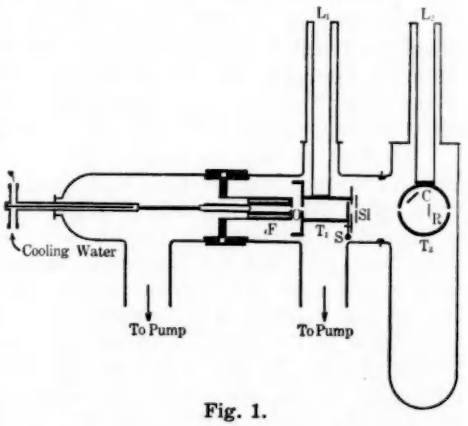


Fig. 1.

(3) J. B. Taylor, *Z. Physik*, **57** (1929), 242.
(4) E. Nishibori, *J. Chem. Soc. Japan*, **58** (1937), 22.

hand. R is a tungsten ribbon 5 cm. long, 5 mm. wide and 0.13 mm. thick and C is a nickel cathode for collecting ions. T_2 is a copper tube cooled by liquid air in L_2 and protects the tungsten ribbon from harmful vapours given off by such as sealing wax.

Galvanometer circuit. This is shown in Fig. 2. The cathode C is kept at 120 V. negative against the tungsten ribbon. G is a ballistic galvanometer made in the Institute of Physical and Chemical Research and has a sensitivity of 3.77×10^{-10} coulombs. The protecting copper tube T_2 is kept at 6 V. positive against the ribbon to prevent ions from coming to it. The ribbon was heated with an alternating current of 10–42 A. taken from the sources of A. C. 100 V. and 200 V. through a step-down transformer. The temperature of the ribbon was measured with a Siemens optical pyrometer.

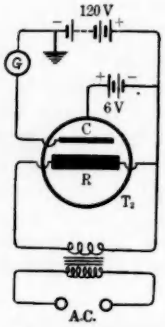


Fig. 2.

The treatment of the tungsten ribbon. As the surface of ordinary tungsten is always stained with alkali salts, it emits their ions when heated. The ribbon must therefore be freed from these by heating repeatedly for about 10 seconds in high vacuum at 1400–1500°C. until practically no ions could be detected by the galvanometer. It may be desirable to heat the tungsten at much higher temperatures but in the present case, heat thus generated causes an undue heating of the apparatus. At any rate the above treatment proved quite satisfactory for the purpose.

Purification of potassium. Potassium used in this experiment was carefully distilled in high vacuum into a long glass tube of appropriate diameter and kept dry for occasional use. When wanted, a short piece of the tube is cut out and immediately introduced into the oven and then the whole apparatus is evacuated without delay.

Method of measurement. When the evacuation is complete a required constant temperature is applied to the oven to produce an atomic beam of a definite intensity. With the shutter kept closed, the ribbon is flashed to remove any freshly adsorbed alkali atoms, left to cool for some time, and then the shutter is opened for a definite time to fire potassium atoms upon the ribbon surface, which is then flashed and the deflection of the ballistic galvanometer is recorded. The time of exposure of the ribbon to the beam is accurately measured with the stop-watch mentioned above. In this measurement we must be sure that all colliding potassium atoms are completely adsorbed by the ribbon. This was ascertained by Taylor and Langmuir[5] in the case of caesium. They showed that as long as the temperature of tungsten is below about 800°K., the impinging atoms are entirely fixed on the tungsten, until a mono-atomic layer is formed. It may be, therefore considered that it is the same in the present case.

Results. *Uniformity of the ribbon surface.* The ionizing power of the hot ribbon surface may differ near the two ends because of unequal

(5) J. B. Taylor and I. Langmuir, *Phys. Rev.*, **44** (1933), 423.

temperature distribution. Therefore, at least the uniform ionizing power of the portion which is uniform in temperature must be ascertained, if that part should be used for the intensity measurement. For this purpose the middle part of the ribbon which was to receive the atomic beam was shifted sideways by a special device not shown in the figure, exposing thereby different parts of the surface to the beam. The result obtained is shown in Fig. 3. The abscissa shows the displacement of the ribbon, while the ordinate represents the relative galvanometer deflections referred to position 2. All values agree with one another within a few per cent, showing that the uniformity is well rendered.

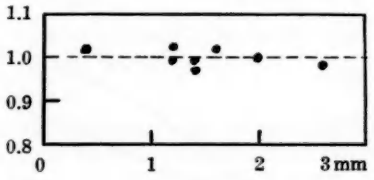


Fig. 3.

Relation between the ribbon temperature and the ionization efficiency. Fig. 4 illustrates the results of our measurements made with the aim to obtain this important relation. The ribbon was exposed to the atomic beam in each case for a definite time. The deflections of the galvanometer resulted by the flashing at different temperatures are shown in the ordinate and the flashing temperature and the corresponding electric current used for the flashing, are indicated in the abscissa. Curve I was obtained with the oven temperature 136°C. and the time of exposure 40 sec., while curve II, with 232°C. and 30 sec. respectively. Obviously the surface concentration of adsorbed atoms is lower in the former case. In both cases the curves rise rapidly until about 800°C., which implies the rapid increase of the ionization efficiency with the rise of temperature. Above 800°C., curve I shows a constant value which suggests the complete ionization of adsorbed atoms, while curve II has a maximum. This may be explained by the combined effect of the high surface concentration of adsorbed atoms and the surface migration which will be fully described in the next report.

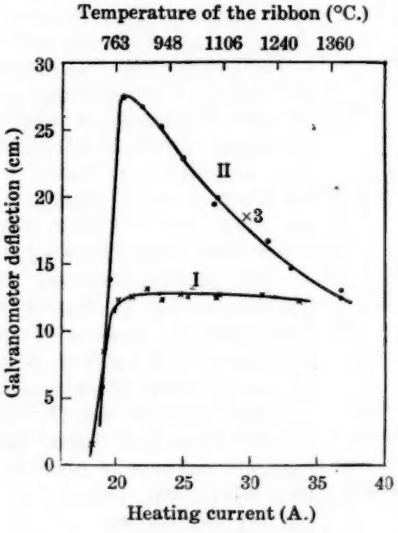


Fig. 4.

Relation between the surface concentration of adsorbed atoms and the ionization efficiency. When applying this method of flashing to the intensity measurement of an atomic beam, it is of the utmost importance to know the influence of the surface concentration of adsorbed atoms upon the ionization efficiency. The following experiment will make this point clear.

An atomic beam of a constant intensity was produced and the time of exposure of the ribbon to it was varied. The surface concentration of adsorbed atoms thus obtained is proportional to the time of exposure, since the condensation coefficient may be assumed to be unity. The ribbon with adsorbed atoms was then flashed and the deflection of the galvanometer was noted. The results obtained are shown in Figs. 5 and 6, where the time of exposure is indicated in the abscissa and the galvanometer deflections in the ordinate. Curves I–V represent the results obtained with five different beam intensities, corresponding to respective oven temperatures. Each curve rises linearly until the galvanometer deflection becomes about 19 cm. This suggests that the ionization efficiency is 100 per cent in this range of surface concentration. (Curve III shows a slight deviation from a straight line, but this was found to be due to a small change in the oven temperature in the course of measurement.)

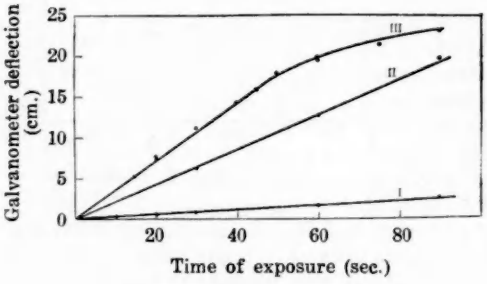


Fig. 5.

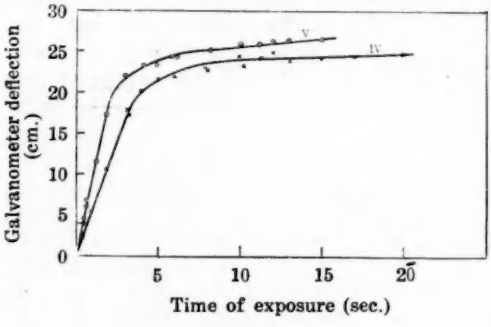


Fig. 6.

In reality, however, if the two curves in Fig. 6 is arranged to one with a smaller inclination (cf. Fig. 7), we see that the straight portion extends hardly to 15 cm. From this value, the highest surface concentration which still permits the perfect ionization of adsorbed atoms may be calculated. The results shown in Figs. 5 and 6 were obtained with deposits from a slightly divergent beam which has passed the last defining hole 3.45 mm. in diameter, perforated in the protector tube, so that the circular deposits formed on the ribbon is a little larger than the hole, namely 3.76 mm.

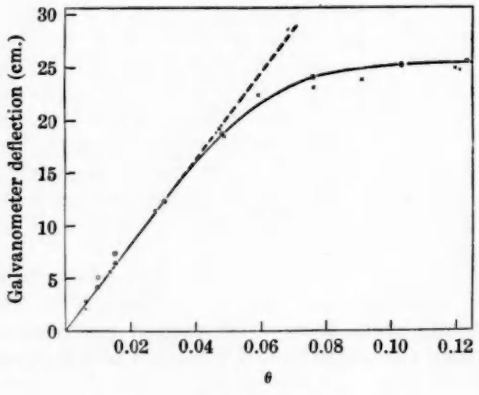


Fig. 7.

in diameter corresponding to the area of 0.111 cm.^{2}. According to Taylor and Langmuir[5] the number of caesium atoms in the mono-atomic layer on tungsten is 4.8×10^{14} per cm.^{2} of the apparent surface. This number is also applicable in the case of potassium. If we assume that the maximum surface concentration allowable for perfect ionization corresponds to 15 cm. of the galvanometer deflection, the number of ions which causes this deflection will be

$$\frac{150 \times 3 \times 3.77 \times 10^{-10} \times 2}{1.6 \times 10^{-19}} = 2.12 \times 10^{12},$$

where 3.77×10^{-10} is the sensitivity of the galvanometer which was used at 1/3 of its full sensitivity by means of an Ayrton shunt and the mirror-scale distance was one half of the normal, 1.6×10^{-19} is the ionic charge expressed in coulomb. Since so many ions were adsorbed on the apparent surface of 0.111 cm.^{2}, the fraction θ covered by the mono-atomic layer must be

$$\theta = \frac{2.12 \times 10^{12}}{0.111 \times 4.8 \times 10^{14}} = 0.040.$$

According to Langmuir,[6] if ν_p and ν_a are respectively the numbers of ions and atoms evaporated in unit time from unit area of the surface which is in equilibrium with the impinging atoms, their ratio may be given by

$$\frac{\nu_p}{\nu_a} = \frac{1}{2} \exp. \left[\frac{\varepsilon(V_w - V_i - V_c)}{kT}\right] \qquad (1).$$

V_w is the work function of pure tungsten and V_i the ionization potential of potassium and V_c the contact potential of tungsten covered with potassium against pure tungsten. V_c varies with θ. Now in the course of flashing at a temperature T, the surface concentration and consequently the contact potential, change continuously. Equation (1) holds only for a minimum amount of potassium atoms evaporated. Let us define the differential ionization efficiency for the surface with a certain θ and V_c by equation (2), where $N = \nu_p + \nu_a$:

$$\frac{d\nu_p}{dN} = \frac{\frac{1}{2} \exp. \left[\frac{\varepsilon(V_w - V_i - V_c)}{kT}\right]}{1 + \frac{1}{2} \exp. \left[\frac{\varepsilon(V_w - V_i - V_c)}{kT}\right]} \qquad (2).$$

This equation shows that the ionization efficiency is highest when V_c is nil and decreases as V_c increases.

The total ionization ν_p which is proportional to the galvanometer deflection may be obtained by integrating equation (2) with respect to θ from θ to zero, N and V_c being expressed in terms of θ. N is obviously equal to $N_0\,\theta$, where $N_0 = 4.8 \times 10^{14}$ is the number of atoms in 1 cm.^{2} of the mono-atomic layer on tungsten. If V_c is assumed to be proportional to

(6) I. Langmuir, *J. Am. Chem. Soc.*, **54** (1932), 2825.

θ, i.e. $V_c = c\theta$, as will be discussed below, the integration gives

$$\nu_p = AN_0\frac{kT}{c\varepsilon}\Big[\log\,(1+\frac{1}{2}\exp.\,[\varepsilon(V_w-V_i)/kT])- \log\,(1+\frac{1}{2}\exp.\,[\varepsilon(V_w-V_i-c\theta)/kT])\Big] \qquad (3),$$

where $A = 0.111$ cm.^{2} the area of the deposit.

We see from this equation that the total ionization will show a linear increase for a considerably wide range of θ, if $V_w - V_i$ is so large that 1 can be neglected against the expotential term, for in this case equation (3) is reduced to $\nu_p = N_0\,\theta$. This means the complete ionization for this range of θ.

The general form of the curve is determined solely by the second term, which can be put in the form $\log(1+e^x)$ and is graphically represented in Fig. 8. The comparison with the experimental curve (Fig. 7) shows that its linear portion corresponds to the range of x from 4 to 2, an appreciable deviation from the linearity beginning at about 2, or at

$$\varepsilon(V_w - V_i - V_c)/kT = 2.$$

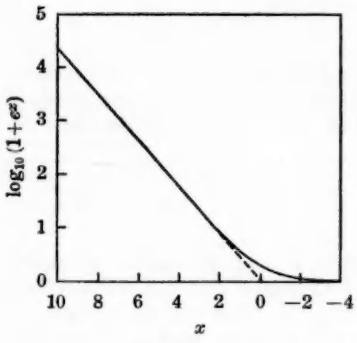


Fig. 8.

Now if we put in equation (2) $V_w = 4.52$ V. $V_i = 4.32$ V. $T = 1.379°$K. and $V_c = 0$, the ionization efficiency will be found considerably less than 100 per cent:

$$\frac{\nu_p}{N} = 0.804\,.$$

Thus the value of $V_w - V_i$ is not large enough to explain the straight portions of the curves shown in Figs. 5 and 6.

In their experiments on the surface ionization of potassium by tungsten, Copley and Phipps[7] found that the values of ν_p/ν_a which they found could be brought into conformity with equation (1) if the factor $\frac{1}{2}$ was omitted.

As they pointed out, a factor $(1-r_p)/(1-r_a)$ has been omitted in equation (1), where r_p and r_a are the reflection coefficients of ions and atoms. This factor is usually supposed to be unity but they assumed that it happened to cancel the factor $\frac{1}{2}$. This argument may not be accepted as it stands but the omission of $\frac{1}{2}$ has the favourable effect of increasing the ionization efficiency. According to equation (3) the differential ionization efficiency is calculated to 89.2 per cent at $\theta = 0$. This value is, however, still too low to explain the experimental results. Further considerations in this point will be discussed in the next report.

(7) Copley and Phipps, *Phys. Rev.*, **45** (1934), 344.

Summary.

In these experiments on the measurement of the intensity of potassium atomic beams with a tungsten ribbon, the following results have been obtained:

(1) The ribbon was used to catch potassium atoms at room temperature and the positive ions formed by flashing were measured with a ballistic galvanometer.

(2) The ribbon surface is uniform for the ionization of potassium atoms.

(3) For the evaporation in the form of ions of adsorbed potassium atoms, the ribbon must be heated higher than 800°C.

(4) When the ionization of adsorbed potassium atoms is effected by flashing, the ionization is complete, when the surface concentration is below 0.04; otherwise, the ionization is incomplete.

(5) The ionization efficiency as a function of the surface concentration of potassium atoms was calculated on simple assumption and was found to deviate from the value observed.

The author wishes to express his sincere thanks to Prof. Nobuji Sasaki for his kind suggestion. Thanks are also due to the Japan Society for the Promotion of Scientific Research for a grant to Prof. Sasaki, from which the expense has been defrayed; to Dr. T. Okada, Institute of Chemical Technology; to Mr. B. Imamura, of the Tokyo Denki Kabushiki Kaisha, for supplying him with tungsten ribbons; and to Professor C. Matsuda, Institute of Electrical Engineering for lending him an optical pyrometer.

Laboratory of Inorganic Chemistry,
Department of Science,
Kyoto Imperial University.

On the Catalytic Decomposition of Oxalic Acid by Colloidal Platinum-carbonyl.

By Isamu SANO.

(Received March 13, 1939.)

Introduction. It is generally accepted through experiences[1] for a long time, although there have been raised a number of objections[2] against the concept, that oxalic acid is decomposed in its aqueous solutions

(1) G. Bizio, *Z. anal. Chem.*, **9** (1870), 392; A. Downes and T. P. Blunt, *Proc. Roy. Soc.* (London), **29** (1879), 219; E. Duclaux, *Compt. rend.*, **103** (1886), 1011; K. Wehmer, *Botan. Ztg.*, **1891**, 49; *Chem. Zentr.*, **62** (1891), II, 476; **63** (1892), I, 171; A. Richardson, *J. Chem. Soc.*, **65** (1894), 450; H. de Vries, *Z. angew. Chem.*, **1899**, 521; W. P. Jorissen, *Z. angew. Chem.*, **1899**, 521.

(2) T. Gigli, *Chem. Zentr.*, **64** (1893), I, 11.

by oxygen in the air to turn into carbon dioxide and water, if exposed to direct sun-light as well as (naturally in smaller extent) to diffused day-light for a certain space of time; while if not subjected to the agency of light (for instance, in the dark), it is quite stable.

It is thoroughly known as well, on the other hand, that oxalic acid is decomposed in its aqueous solutions by moulds,[3] no matter whether it may be present in the dark or in the light, and according to Wehmer[3] and Jorissen,[1],[3] the acid acts as a poison for the moulds if the concentration of the acid solution is greater than 2–3%. Dilute solutions can be conserved by means of sterilization or by adding 50 c.c. of concentrated sulphuric acid per litre, boric acid being scarcely effective. On the addition of manganese sulphate the decomposition of oxalic acid due to oxidation in its aqueous solutions is more accelerated in the presence of light.

S. Ishimaru[4] investigated the influences of purity of oxalic acid preparation, day-light, and sulphuric acid added on the preservation of aqueous solutions of oxalic acid during a long period extending over seven months, and established that a 0.01 N solution is stable when 50 c.c. of concentrated sulphuric acid per litre is added, irrespective of purity of preparation as well as day-light. A 0.1 N solution is decomposed in the light notwithstanding the addition of sulphuric acid, but stable in the dark without sulphuric acid. A 0.5 N solution is stable in the dark without sulphuric acid, solution of pure preparation being stable in the light.

O. Šulc[5] studied the effects of various metals in finely divided state such as palladium, silver, copper, and platinum on the decomposition of aqueous solutions of oxalic acid at room temperatures. The results obtained with palladium which was ascertained to be the most effective of the metals aforesaid, are tabulated below. A 100 c.c. of 0.1 N aqueous oxalic acid solution was mixed with 1.36 grams of palladium powder afresh ignited and cooled in the air prior to use in a closed flask in each run of the experiments and 10 c.c. was pipetted out from it at the desired inter-

Time elapsed in days	Titre of the oxalic acid solution in c c.			
	in the dark		in the light	
	without palladium	with palladium	without palladium	with palladium
0	10.05	10.05	10.04	10.04
4	—	—	9.92	8.62
8	10.03	8.79	—	—
9	—	—	9.00	6.78
19	10.00	8.24	6 40	3.75
26	9.90	8.31	—	—
38	—	—	0.34	0.25

(3) C. Neubauer, *Z. anal. Chem.*, **9** (1870), 392; W. N. Hartley, *Chem. News*, **37** (1878), 9; G. Fleury, *Chem. Zentr.*, **14** (1883), 547; O. Warburg, *Untersuch. botan. Inst. Tübingen*, **2** (1886-8), 117; K. Wehmer, *Botan. Ztg.*, **1891**, 49; *Chem. Zentr.*, **62** (1891), II, 476; **63** (1892), I, 171; W. P. Jorissen, *Z. angew. Chem.*, **1899**, 521.

(4) S. Ishimaru, *J. Chem. Soc. Japan*, **43** (1922), 767; **53** (1932), 449; *Science Repts. Tôhoku Imp. Univ.*, Ser. I, **24** (1935), 411.

(5) O. Šulc, *Z. physik. Chem.*, **28** (1899), 719.

vals of time, mixed with a small quantity of sulphuric acid, warmed if necessary and titrated with a potassium permanganate solution.

In the preceding papers,[6] the author reported the formation and behaviour of a platinum-carbonyl sol of red colour obtainable from an aqueous solution of chloroplatinic acid by the action of carbon monoxide and the catalytic decomposition of hydrogen peroxide by the sol. The present communication deals with the experiments on the decomposition of oxalic acid in its aqueous solutions due to oxidation by the air, which is catalysed by the colloidal platinum-carbonyl as well as by the colloidal platinum obtainable from it.

On passing carbon monoxide through an aqueous solution of chloroplatinic acid at ordinary temperature for a while, the colour of the solution changes from yellow to red, the platinum-carbonyl sol being thus obtained. By dialyzing the red sol or letting it stand in the air, it turns black before long to produce a platinum sol as prepared by Bredig's method.

Experimental Procedures and Results. The oxalic acid solutions used were prepared by dissolving oxalic acid purified by means of recrystallization in distilled water. The red sol was prepared by passing carbon monoxide through a 0.05% aqueous solution of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) with nearly a constant velocity throughout the experiments, carbon monoxide being obtained by heating the mixture of oxalic acid and concentrated sulphuric acid and purified by passing through alkaline hydroxide solutions. The black sol was obtained from the red one by standing it in the air as already mentioned. Accordingly the sol, red or black, was inferred from calculation to contain 0.188 grams of platinum in one litre.

In each run of the experiments described below, the red sol and the black one added as catalyst are respectively used immediately after its formation, the red sol being obtained from the aqueous solution of chloroplatinic acid and the black one from the red sol, and both of them being not dialyzed.

The reactions were carried out at 25.0°C. as well as 50.0°C. under diffused day-light. The vessels were cleand and steamed to the full before use. The results obtained are indicated in Table 1 to Table 12, where t denotes the time elapsed from the beginning in hours, c the titre of the reacting solution titrated with a 0.1 N barium hydroxide solution at time t in c.c., corrections being made for the portion of the titre attributable to hydrochloric acid in the sol added as catalyst, and t_r the time duration during which the sol remains red in the reaction mixture before it passes into black in hours. The meanings of c_k and t_k will be explained later. The procedures and results were as follows.

25.0°C.: A 20 c.c. of a 0.10 N oxalic acid solution was placed in a flask, 20 c.c. of the red sol was added to it and the solution thoroughly mixed by shaking. At the desired intervals of time, 10 c.c. was pipetted out from it and titrated with the barium hydroxide solution. The results are shown in Tables 1 and 2.

(6) I. Sano, this Bulletin, **9** (1934), 320; **13** (1938), 118.

Table 1.

t	c	c_k ($t_k = 14$)
0	11.80 (c_0)	—
2	11.75	—
4	11.78	—
6	11.80	—
27	11.71	11.76
29	11.69	11.75
50	11.59	11.74
75	11.50	11.75
99	11.43	11.77
147	11.32	11.85
173	11.23	11.86
197	11.08	11.80
221	10.92	11.73
245	10.84	11.74
317	10.64	11.81
365	10.56	11.92
412	10.30	11.82
604	9.62	11.79
$t_r = 3$		

Table 2.

t	c	c_k ($t_k = 6$)
0	14.14 (c_0)	—
4	14.13	—
5	14.15	—
24	13.96	14.10
50	13.81	14.17
55	13.76	14.15
72	13.63	14.16
75	13.56	14.11
96	13.41	14.12
100	13.40	14.14
120	13.23	14.12
168	12.89	14.14
172	12.83	14.11
192	12.70	14.13
194	12.68	14.12
216	12.48	14.08
220	12.49	14.12
264	12.14	14.08
$t_r = 4$		

50.0°C.: The reacting mixtures consisting of 10 c.c. of aqueous solution of oxalic acid of a definite concentration and 2 c.c. of the red or black sol were placed in test-tubes provided with rubber stopper through which a capillary tube was inserted as a line of communication of the air. At the desired intervals of time, the test-tubes were, by turns, titrated with the barium hydroxide solution. The reacting solutions were, as in the other cases, agitated at short intervals. The results are given in Tables 3, 4, 5, 6, 7 and 8.

Table 3. Concentration of oxalic acid solution : 0.10 N
Sol added as catalyst : red

t	c	c_k ($t_k = 6$)
0	15.69 (c_0)	—
1.5	15.79	—
3	15.62	—
6	15.48	—
9	15.39	15.46
12	15.34	15.48
15	15.25	15.46
18	15.19	15.47
21	15.16	15.51
24	15.05	15.47
27	14.97	15.45
30	14.91	15.46
$t_r = 2$		

Table 4. Concentration of oxalic acid solution : 0.10 N
Sol added as catalyst : red

t	c	c_k ($t_k = 10$)
0	12.06 (c_0)	—
2	12.13	—
4	11.95	—
6	11.82	—
8	11.71	—
10	11.59	—
12	11.55	11.60
16	11.45	11.60
20	11.34	11.59
24	11.17	11.52
28	11.16	11.61
32	11.05	11.60
35	10.98	11.60
$t_r = 2$		

Table 5. Concentration of oxalic acid solution : 0.10 N
Sol added as catalyst : black

t	c	$c_k (t_k = 2)$
0	12.07 (c_0)	—
1	11.80	—
2.5	11.57	11.61
4	11.45	11.60
6	11.35	11.64
9	11.02	11.52
12	10.87	11.58
16	10.70	11.69
21	10.35	11.67
24	10.12	11.63
28	9.80	11.55
30	9.77	11.67
	$t_r = -$	

Table 6. Concentration of oxalic acid solution : 0.05 N
Sol added as catalyst : red

t	c	$c_k (t_k = 2)$
0	5.65 (c_0)	—
2	5.69	—
4.5	5.42	5.61
6	5.32	5.60
8	5.25	5.69
10	5.10	5.68
12	4.91	5.62
16	4.73	5.71
21	4.39	5.67
24	4.11	5.53
27	4.05	5.67
32	3.76	5.64
	$t_r = 2$	

Table 7. Concentration of oxalic acid solution : 0.05 N
Sol added as catalyst : black

t	c	$c_k (t_k = 2)$
0	6.12 (c_0)	—
1	5.88	—
2.5	5.64	5.70
4	5.54	5.76
6	5.30	5.73
9	4.97	5.70
12	4.78	5 81
16	4.33	5.70
21	4.02	5.83
24	3.73	5.74
27	3.52	5.74
30	3.38	5.85
	$t_r = -$	

Table 8. Concentration of oxalic acid solution : 0.025 N
Sol added as catalyst : red

t	c	$c_k (t_k = 2)$
0	3.05 (c_0)	—
2	3.10	—
4	2.84	3.05
6	2.68	3.10
8	2.50	3.11
10	2.31	3.08
12	2.16	3 10
16	1.87	3.10
21	1.79	3.56
24	1.35	2.99
27	1.27	3.13
30	1.12	3.08
	$t_r = 2$	

One run was carried out at 50.0°C. in hermetically sealed test-tubes. The results obtained are indicated in Table 9.

With the view of investigating the extent to which the light has influence upon the decomposition of oxalic acid in its aqueous solution, a number of runs were made under the conditions as already described without the sol being added. The results are shown in Tables 10, 11 and 12. From these results it can be concluded that aqueous solutions of oxalic acid are not decomposed in the least under the conditions concerned.

Table 9. Concentration of oxalic acid solution : 0.05 N
Sol added as catalyst : black

t	c	c_k ($t_k = 1.5$)
0	6.07 (c_0)	—
1	5.79	—
2.5	5.69	5.76
4	5.54	5.72
6	5.38	5.70
9	5.24	5.78
12	4.98	5.71
20	4.75	—
24	4.72	—
27	4.66	—
30	4.66	—
	t_r = —	

Discussion of the Results. The above results indicated in the tables (Table 1 to Table 9 inclusive) are graphically depicted below in terms of the relationship between $\log(c_0/c)$ and t in Fig. 1, 2, 3 and 4 (Curve 1 to Curve 9 inclusive). If the decomposition of oxalic acid due to oxidation in its aqueous solutions, which is accelerated by colloidal platinum-carbonyl as well as colloidal platinum should, in the course of reaction, come to proceed in accordance with the formula for unimolecular reaction

$$-dc/dt = kc \quad \text{or} \quad \log(c_0/c) = kt,$$

where c_0 is the initial concentration and k the velocity constant, it may be anticipated that there must be a portion of straight line in the curve indicating the relation between $\log(c_0/c)$ and t.

Table 10.
Concentration of oxalic acid solution : 0.10 N
Temperature : 25.0°C.

t	c
0	14.32 (c_0)
20	14.31
24	14.31
43	14.28
68	14.27
72	14.36
92	14.40
96	14.37
116	14.35
164	14.35
188	14.38
216	14.38
260	14.36
356	14.35
358	14.34
456	14.29
457	14.30

Table 11.
Concentration of oxalic acid solution : 0.10 N
Temperature : 50.0°C.

t	c
0	12.17 (c_0)
4	12.16
9	12.12
12	12.16
18	12.15
24	12.17
30	12.12

Table 12.
Concentration of oxalic acid solution : 0.05 N
Temperature : 50.0°C.

t	c
0	6.14 (c_0)
4	6.15
9	6.22
12	6.16
18	6.18
24	6 16
30	6.16

In the case where the red sol is added as catalyst, the apparent concentration of oxalic acid solution remains nearly constant over a certain space of time and the reacting solution is of red tint throughout the period, suggesting the sol to exist unchanged. In time, however, the solution will lose the red colour to become tinged with black and then the decomposition will begin abruptly and proceed smoothly. The induction period

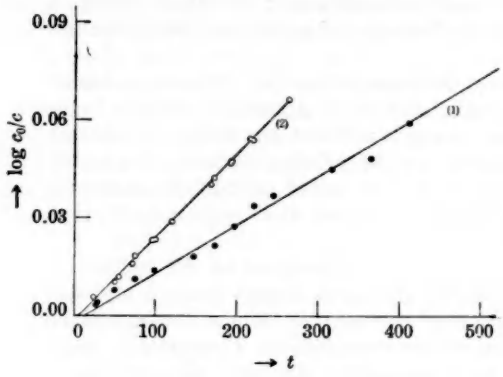


Fig. 1.

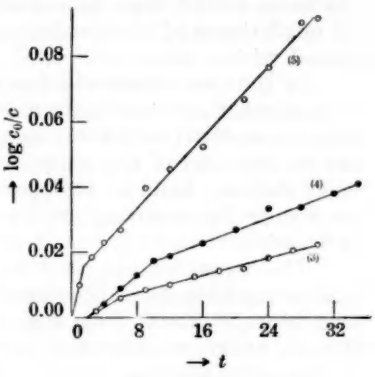


Fig. 2.

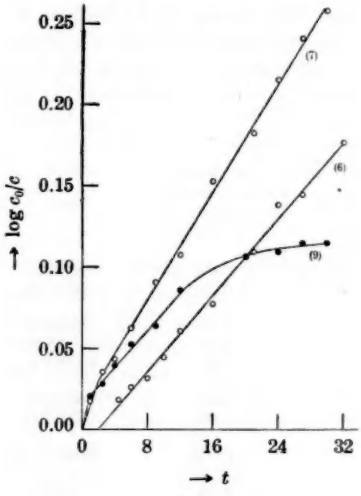


Fig. 3.

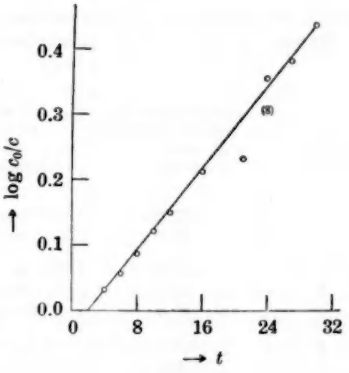


Fig. 4.

mentioned above is distinctly shown by the former parts of Curves 1, 2, 3, 4, 6 and 8; while the latter parts of the curves concerned are linear, indicating the reaction to proceed as unimolecular.

On adding the red sol to aqueous solutions of oxalic acid, carbon monoxide ratiocinated from various facts already established[7] to be held in the colloidal particle as its essential constituent will vanish gradually from it through volatilization as well as oxidation, since the sol is diluted with oxalic acid solution loaded with dissolved oxygen. Sooner or later, carbon monoxide constituting the particle will reach a certain limiting amount, when the particle may be reasonably regarded as colloidal

(7) I. Sano, this Bulletin, **9** (1934), 320.

platinum rather than as colloidal platinum-carbonyl; in other words, a sol of platinum of black colour will be formed and hereupon, the induction period will be over.

In the case where the black sol obtained from the red one is added as catalyst, the decomposition of oxalic acid in its aqueous solutions takes place immediately after mixing and proceeds without any delay. Although the former part of the curve standing for the relation between $\log(c_0/c)$ and t makes a bend in due course of time, the latter part of it assumes a rectilinear figure during the time duration concerned as shown by Curves 5, 7 and 9.

The transition period above mentioned—in the case of the red sol, it follows in the wake of the induction period as seen from Curves 3 and 4—may probably result from coagulation of the sol due to electrolyte. Since the sol under consideration is negatively charged, its coagulation must be caused by positive charge and in consequence, the catalytic activity of colloidal particles must be decreased to some extent. On passing this stage, there may scarcely occur any change in the catalytic activity of the particles. The coagulation may be assumed to proceed the more rapidly as well as strongly, the more concentrated the oxalic acid solution is.

This can be seen by comparing one another the magnitudes of the velocity constant, k, for the straight portion of the curve, calculated from the diagram. It is clear from the table that k increases definitely as the

Number of table	Temperature at which the reaction was carried out (°C.)	Sol added as catalyst	t_r	Concentration of aqueous solution of oxalic acid (N)	k (hour^{-1})
1	25.0	red	3	0.10	0.000150
2	25.0	red	4	0.10	0.000249
3	50.0	red	2	0.10	0.000658
4	50.0	red	2	0.10	0.000956
5	50.0	black	—	0.10	0.00275
6	50.0	red	2	0.05	0.00586
7	50.0	b'ack	—	0.05	0.00850
8	50.0	red	2	0.025	0.0157
9	50.0	black	—	0.05	0.00563

concentration of aqueous solution of oxalic acid decreases. It was observed, in fact, at 50.0°C. that in dilute solutions, the sol added is practically stable and remains black as it was throughout one run of the experiments; while in concentrated solutions, it coagulates to a marked degree in several hours from the commencement to settle at the bottom. Consequently, it appears that coagulation of the sol may be more influenced by electrolyte than by heat.

The value of c_k tabulated previously was calculated from k thus obtained in accordance with the formula for unimolecular reaction

$$\log(c_k/c) = kt,$$

where c is the concentration of oxalic acid solution at time t elapsed from a specified starting-point of reckoning indicated by t_k in the tables. It might be anticipated for c_k to assume a constant value in each run of the experiments if the reaction should proceed as unimolecular.

It has been stated already that oxalic acid is decomposed in its aqueous solutions in the presence of oxygen. The effect can be seen distinctly from Curve 9. In this run the reaction was carried out in test-tubes hermetically sealed in order to keep out the air from the outside. It can be seen that drift occurs in the final stage from want of oxygen.

In connection with what has been mentioned above, some theoretical consideration will be made as follows.

It may be supposed on the whole that chemical reactions will occur between molecules adsorbed on adjacent spaces of the catalyst surface, and the rate of reaction is slow in comparison with the rate at which molecules of reactants condense upon and evaporate from the surface; that is to say, the rate of reaction will not affect to any appreciable extent the equilibrium between the adsorbed layer and the surrounding medium.

If θ_1 represents the fraction of the available surface covered unimolecularly with molecules of oxalic acid and θ_2 with molecules of oxygen at any instant, it will follow that for equilibrium between the adsorbed layer consisting of both molecules of oxalic acid as well as oxygen and those in the surrounding medium, under the assumption that each molecule of these may occupy one elementary space of the surface and the presence of solvent may be left out of consideration,

$$\alpha_1\mu_1(1-\theta_1-\theta_2) = \nu_1\theta_1 \quad \text{and} \quad \alpha_2\mu_2(1-\theta_1-\theta_2) = \nu_2\theta_2\,,$$

α_1 and α_2 being the fractions of the numbers of molecules of oxalic acid and oxygen, μ_1 and μ_2, striking the surface in unit time which condense, and $\nu_1\theta_1$ and $\nu_2\theta_2$ the numbers of molecules of oxalic acid and oxygen which evaporate from the surface in unit time. Reference must be made to that oxalic acid may be treated as non-electrolyte for the sake of simplicity, the state of the molecule adsorbed on the catalyst surface being not taken into consideration both for dissociated as well as undissociated molecule.

If the surface is covered so sparsely by molecules of both of them that $\theta_1 \ll 1$ and $\theta_2 \ll 1$ and accordingly $\theta_1+\theta_2 \ll 1$, then $1-\theta_1-\theta_2$ may be put as approximately equal to unity; hence, it follows that

$$\alpha_1\mu_1 = \nu_1\theta_1 \qquad \text{and} \qquad \alpha_2\mu_2 = \nu_2\theta_2$$

or

$$\theta_1 = \mu_1\cdot\alpha_1/\nu_1 \qquad \text{and} \qquad \theta_2 = \mu_2\cdot\alpha_2/\nu_2\,.$$

Since it may be presumed for the rate of reaction, v, to be proportional to the amounts of reactants adsorbed on the available surface, it will be given by

$$v = k\theta_1\theta_2\,,$$

k being the velocity constant. Substituting the valeus for θ_1 and θ_2, it follows that

$$v = k_{\mu_1\mu_2} \cdot \alpha_1\alpha_2/\nu_1\nu_2 .$$

Considering μ to be proportional to the concentration, c, of the reactant, this may be written in the form

$$v = k' c_1 c_2 ,$$

k' being made up of a combination of various constants such as k, α and ν. The formula thus obtained reduces to the formula for unimolecular reaction

$$v = k'' c_1 ,$$

where $k'' = k' c_2$, provided that c_2 is constant throughout the experiment, and this is actually the case as the reacting system is supplied with oxygen from the outside.

On studying the influence of light on the decomposition of oxalic acid in its aqueous solutions due to oxidation by oxygen in the air, Richardson[1] concluded that during the decomposition of the acid in the presence of light and oxygen, the carbon in each molecule is oxidized to carbon dioxide and the hydrogen to hydrogen peroxide, if oxygen is in excess, in accordance with the equation

$$C_2O_4H_2 + O_2 = 2\,CO_2 + H_2O_2 ,$$

although the peroxide found by analysis falls, in general, far short (it rarely reaching one-tenth) of that calculated from the equation, on account of the docomposition of the acid occurring at the expense of the peroxide to some extent.

From the above-mentioned, the decomposition of oxalic acid due to oxidation in its aqueous solutions by colloidal platinum will be explained in the following manner. Whenever oxalic acid is decomposed by oxygen on the catalyst surface to produce carbon dioxide and hydrogen peroxide, atomic oxygen will be liberated then and there from hydrogen peroxide since it is readily decomposed by colloidal platinum as a well-known fact, and in quick succession, this will act on molecules of oxalic acid adsorbed on adjacent spaces of the catalyst surface and oxidize them; namely,

$$C_2O_4H_2 + O_2 = 2\,CO_2 + H_2O_2 \qquad \text{(slow)}$$

$$H_2O_2 = H_2O + O \qquad \text{(rapid)}$$

$$O + C_2O_4H_2 = 2\,CO_2 + H_2O \qquad \text{(rapid)}$$

Hence, the reaction

$$2\,C_2O_4H_2 + O_2 = 4\,CO_2 + 2\,H_2O$$

will proceed unimolecularly.

Summary.

(1) The decomposition of aqueous solutions of oxalic acid (0.10, 0.05, 0.025 N) due to oxidation accelerated by colloidal platinum-carbonyl of red colour as well as colloidal platinum of black colour obtainable from

it was, in the presence of oxygen and diffused day-light, studied during a period extending several hundred hours at 25.0°C. and thirty hours at 50.0°C.

(2) In the case where the red sol is added as catalyst, the reaction proceeds as unimolecular after it passed through an induction period and subsequently a transition period, while in the case where the black sol is added, it proceeds as the above after a transition period, no induction period presenting itself.

(3) The more dilute the acid solution, the more stable is the sol throughout the course of the experiment and consequently, the larger is the velocity constant.

(4) The mechanism of the reaction was discussed on these facts.

The author wishes to express his sincere thanks to Prof. J. Sameshima for his kind guidance and encouragement throughout the work. The expense of it has been defrayed from the Committee on Catalysis in the Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

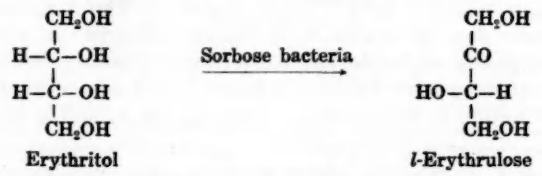
Chemical Institute, Faculty of Science,
Tokyo Imperial University.

The Formation of *d*-Erythrulose.

By Koichi IWADARE.

(Received March 13, 1939.)

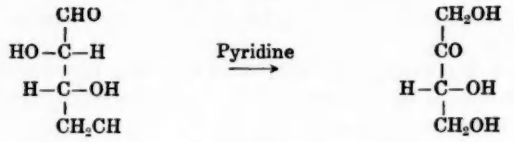
The syntheses of monoses were recently much investigated, and all the aldo- and keto-sugars of hexoses and pentoses, whose existence is supposed by theory, have already been prepared. As for tetroses, among the six theoretically possible forms, *d*-erythrulose has been the only sugar hitherto not synthetized. Its antipode, *l*-erythrulose, or *l*-2-keto-tetrose, was prepared by G. Bertrand[1] by oxidative fermentation of erythritol with sorbose bacteria (*bacterium xylinum*) about forty years ago, and its crystalline derivative was prepared by H. Müller, C. Montigel and T. Reichstein[2] in recent year. This biochemical method, however, is of course unavailable for the formation of *d*-form.



(1) G. Bertrand, *Compt. rend.*, **130** (1900), 1330. In this literature the sugar is written as *d*-erythrulose by old nomenclature, but it is quite clear from the reduction product that it should be *l*-form.

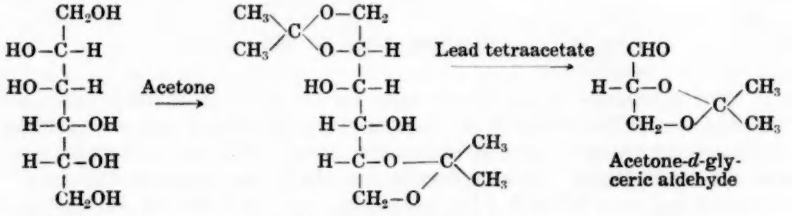
(2) H. Müller, C. Montigel, and T. Reichstein, *Helv. Chim. Acta*, **20** (1937), 1468.

In general, aldoses can be partly transformed to ketoses by heating them with organic bases such as pyridine or quinoline.[3] So *d*-threose was heated with pyridine at various temperatures in order to obtain *d*-erythrulose by epimerization. However, the mixture soon became quite dark, and *d*-erythrulose could not be obtained by this way.



d-Threose *d*-Erythrulose

So the method of R. Prince, K. Gätzi, and T. Reichstein[4] for preparing ketose by the addition of diazo-methane on the acetone derivative of glyconic acid chloride, which has one carbon atom less than the ketose to be obtained, was used successfully for this preparation of *d*-erythrulose. For this purpose, first of all, acetone-*d*-glyceric aldehyde is prepared from *d*-mannitol according to the method of H. O. L. Fischer and E. Baer.[5] That is, *d*-mannitol is shaken mechanically with acetone adding hydrochloric acid for condensing agent, then the mixture is neutralized with lead carbonate, and, after the removal of the solvent by distillation, 1,2,5,6-diacetone-*d*-mannitol is separated from triacetone-mannitol. The former is oxidized with lead-tetraacetate, and thus acetone-*d*-glyceric aldehyde is obtained, the boiling points of which are 54° at 12 mm. and 63° at 20 mm.



d-Mannitol 1,2,5,6-Diacetone-*d*-mannitol

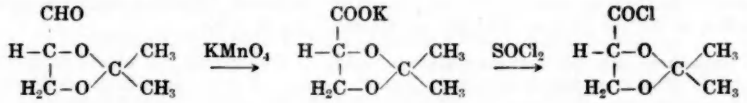
Acetone-*d*-glyceric aldehyde thus prepared is oxidized by potassium permangante in alkaline solution, and the potassium salt of acetone-*d*-glyceric acid is obtained in colourless crystalline powder. Its specific rotatory power is $[\alpha]_D^{15} = +23.7°$ ($c = 2.11$ in water). The potassium salt of acetone-*d*-glyceric acid is heated with thionyl chloride in ether solution and acetone-*d*-glyceric acid chloride is obtained. Freshly distilled chloride has specific rotatory power $[\alpha]_D^{15} = +14.9°$ ($c = 1.6$ in ether). Acetone-*d*-glyceric acid amide is prepared by pouring the chloride into ammonia

(3) S. Danilow, E. V. Danilowa, and P. Schantorowitsch, *Ber.*, **63** (1930), 2271; K. Iwadare and B. Kubota, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **34** (1938), 183.

(4) K. Gätzi and T. Reichstein, *Helv. Chim. Acta*, **21** (1938), 186; R. Prince, Diss. Zürich, 1937.

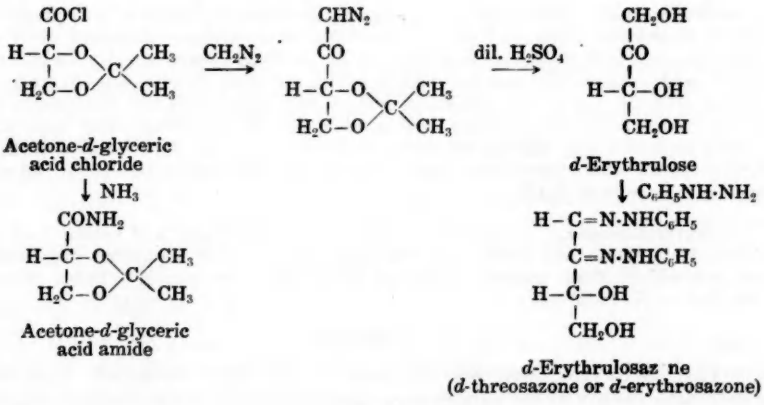
(5) H. O. L. Fischer and E. Baer, *Helv. Chim. Acta*, **17** (1934), 622.

in ether solution. It melts at 72–73° and has specific rotatory power $[\alpha]_D^{16} = +39.1°$ ($c = 0.8$ in water).



Acetone-*d*-glyceric aldehyde — Potassium salt of acetone-*d*-glyceric acid — Acetone-*d*-glyceric acid chloride

Ether solution of acetone-*d*-glyceric acid chloride is slowly poured into diazo-methane solution in ether, cooled with freezing mixture. After a day's standing, the solution is evaporated, and the residual diazo-ketone is submitted to hydrolysis by heating with dilute sulphuric acid. *d*-Erythrulose thus obtained is distilled in vacuo. Colourless syrup with specific rotatory power $[\alpha]_D^{15} = -11 \pm 3°$ in dilute solution. This value is in good agreement with that of *l*-erythrulose ($[\alpha]_D^{15} = +11.4° \pm 1°$), which was reported by H. Müller, C. Montigel, and T. Reichstein.[2] *d*-Erythrulose solution reduces Fehling's solution at once in the cold. Its osazone melts at 168°. (Found: N, 18.64. Calc. for $C_{16}H_{18}O_2N_4$: N, 18.72%). This melting point agrees with that of *d*-threosazone, which was prepared from *d*-threose by the author. So we may be able to say that *d*-erythrulose is now formed.



Acetone-*d*-glyceric acid chloride — Acetone-*d*-glyceric acid amide — *d*-Erythrulose — *d*-Erythrulosazone (*d*-threosazone or *d*-erythrosazone)

Experimental.

Acetone-*d*-glyceric aldehyde. Three hundred grams of *d*-mannitol were mechanically shaken with 6 kg. of acetone and 150 c.c. of concentrated hydrochloric acid for about four hours, excess of lead carbonate or potassium carbonate was added, and the mixture was stirred mechanically. After neutralization, it was filtered, and acetone was removed by distillation. The residual crystalline mass was dissolved in 200 c.c. of alcohol and poured into 2 or 3 litres of water with stirring. The mixture was filtered and evaporated in vacuo, and the residue was dissolved in water. It was again filtered and evaporated. Thus about 100 g. of crude diacetone-mannitol was obtained. It was dissolved in 5 *l.* of petroleum benzine and filtered as soon as the solution was cooled to room temperature. Yield, about 25 g.

Thirty grams of diacetone-*d*-mannitol was dissolved in 1 litre of benzene, and 50 g. of lead tetraacetate was added. After an hour it was filtered and neutralized with diazo-methane, and the greater part of the solvent was removed by distillation. Then it was fractionally distilled at diminished pressure. Acetone-*d*-glyceric aldehyde distilled at 54° at 12 mm., and 63° at 20 mm. Yield, 13 g.

Potassium salt of acetone-*d*-glyceric acid. Ten grams of aldehyde were dissolved in 600 c.c. of water and the solution of 6.5 g. of potassium hydroxide and 10 g. of potassium permanganate in 600 c.c. of water was added drop by drop to it, the mixture being stirred vigorously. After two hours it was filtered, and the filtrate was neutralized with dilute sulphuric acid and evaporated in vacuo to dryness. It was dissolved in absolute alcohol, filtered from inorganic salt, again evaporated to thin syrup, and ether was added to it. Precipitated potassium salt was filtered and recrystallized from alcohol. Its specific rotatory power is $[\alpha]_D^{15} = +23.7°$ ($c = 2.11$ in water). (Found: K, 21.63. Calc. for $C_6H_9O_4K$: K, 21.23%).

Acetone-*d*-glyceric acid chloride. Five grams of potassium salt was suspended in 40 c.c. of ether and 3 g. of thionyl chloride added. The mixture was boiled on a water bath for two hours and filtered. From the filtrate ether and the most of thionyl chloride were removed by distillation, and the residue was fractionally distilled at diminished pressure. The chloride distilled at 61° at 15 mm. It is a clear colourless liquid, with $[\alpha]_D^{15} = +14.9°$ ($c = 1.6$ in ether). Yield, 1 g.

Acetone-*d*-glyceric acid amide. To an excess of etherial solution of ammonia, 0.3 g. of chloride was added. It was then filtered from ammonium chloride and evaporated to syrup. The latter was dissolved in benzene, and soon crystallized. Recrystallized from benzene its melting point was 72–73°. $[\alpha]_D^{16} = +39.1°$ ($c = 0.8$ in water). (Found: N, 9.78. Calc. for $C_6H_{11}O_3N$: N, 9.65%).

***d*-Erythrulose.** One gram of acetone-*d*-glyceric acid chloride was dissolved in 150 c.c. of absolute ether and poured into 1.5 g. diazo-methane dissolved in 60 c.c. of ether, cooling with freezing mixture. After a day's standing, the solution was filtered and evaporated, and the yellow syrup of diazo-ketone was hydrolysed by heating with 100 c.c. of 1% sulphuric acid on the water bath for two hours. Then it was neutralized with freshly precipitated barium carbonate and filtered with active charcoal. The filtrate was evaporated in vacuo to syrup and *d*-erythrulose distilled at 68° at 0.01 mm., the temperature of the bath being 100–105°. Its specific rotatory power was $[\alpha]_D^{15} = -11° \pm 3°$.

***d*-Erythrulosazone.** *d*-Erythrulose was dissolved in water and heated with excess of phenylhydrazine and acetic acid for three hours. The separated oily substance was crystallized from alcohol. Melting point, 168° (Found: N, 18.64. Calc. for $C_{18}H_{18}O_2N_4$: N, 18.72%).

Summary.

(1) *d*-Erythrulose was formed by the hydrolysis of diazo-ketone which was obtained by condensing diazo-methane with acetone-*d*-glyceric acid chloride.

(2) Potassium salt of acetone-*d*-glyceric acid ($[\alpha]_D^{15} = +23.7°$), acetone-*d*-glyceric acid chloride ($[\alpha]_D^{15} = +14.9°$) and acetone-*d*-glyceric acid amide ($[\alpha]_D^{16} = +39.1°$) were obtained.

In conclusion the author wishes to express his hearty thanks to Prof. B. Kubota for his kind advice for this experiment.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

Die Kolloidchemische Untersuchung der Systeme von drei flüssigen Komponenten III.[1] Über Emulgierung zwei-flüssiger Systeme mit gleichen spezifischen Gewichte.

Von Naoyasu SATA und Haruhiko OKUYAMA.

(Eingegangen am 13. März 1939.)

(1) Einleitung. Wenn das spezifische Gewicht disperser Phase und Dispersionsmittels eines disperses Systems gleich wäre, müsste das System theoretisch unendlich betsändig sein.[2] Aber in Wirklichkeit hängen, bekanntlich, noch viele andere Faktoren damit zusammen. Wegen der Leichtigkeit des Experimentes, wurden die Untersuchungen an dieser Richtung meistenfalls mit Emulsionen ausgeführt. So sind z.B. nach Donnan und seine Mitarbeitern,[3] für die Beständigkeit einer Emulsion, ausser der Verschiedenheit der spezifischen Gewichte zwischen disperser Phase und Dispersionsmittel, noch die Viskosität, die Grenzflächenspannung, ζ-Potential usw. massgebend, von denen sie das ζ-Potential am wichtigsten gefunden haben. Bhatnagar[4] hat den Versuch angestellt an Anilin-Wasser System bei 46°C., wo die spezifische Gewichte beider Schichten den gleichen Wert ergeben. Dadurch wurde bestätigt, dass das Vorhandensein kleiner Menge fremder Substanz, als Emulgator oder Stabilisator, die entscheidende Rolle spielt. Während der Experimente vorhergehender Versuche[1] haben wir gefunden, dass es möglich ist, durch Kombinieren geeigneter drei Flüssigkeiten zwei-flüssige Systeme mit gleichen spezifischen Gewichte herzustellen. Mann kann dabei nach Wahl der Komponenten noch Viskosität, Grenzflächenspannung usw. einigermassen willkürlich regulieren. Im folgenden haben wir untersucht die Emulgierungserscheinung und Eigenschaften der Emulsionen, welche aus den Flüssigkeitspaaren gleicher spezifischen Gewichte entstanden sind. Es wurde zum Versuch besonders solche Kombinationen der Komponenten ausgewählt, dass es zwischen ihnen die chemische Reaktion ausgeschlossen ist und dadurch hervorgerufene Nebenwirkung auf Emulsion auch vernachlässigbar ist.

(2) Wahl der Versuchsmaterialien. Berücksichtigend die Mischbarkeit und spezifische Gewichte der Flüssigkeiten, ist es nicht schwer die Kombinationen von drei Flüssigkeiten auszuwählen, welche bei geeigneter Konzentration zwei-flüssige Systeme mit gleicher spezifischen Gewichte ergeben würden. Nachstehendem Versuch haben wir folgende Kombinationen benutzt.

System A: Wasser-Benzol-Tetrachlorkohlenstoff.
System B: Wasser-Amylalkohol (iso)-Chloroform.
System C: Wasser-Methylalkohol-Benzol.

(1) Sata und Kimura, dies Bulletin **10** (1935), 409; Sata und Niwase, *ibid.*, **12** (1937), 86.
(2) W. Clayton, "The Theory of Emulsions and Their Technical Treatment", 121, London (1935).
(3) *ibid.*, 27.
(4) Bhatnagar, *Trans. Faraday Soc.*, **16** (1921), Appendix, 27.

Da die Grenzflächenspannung zwischen nicht mischbaren Flüssigkeiten an vielen Beispielen bekannt sind,[5] könnte man die Grenzflächenspannung nach dem Zufügen dritter Flüssigkeit ordnungsmässig abschätzen und zwar in obengenannten Systemen sollte die Reihenfolge der Grenzflächenspannung: A>B>C sein. Es wurde die Vermutung tatsächlich experimentell bestätigt, wie in Tabelle 1 zu ersehen sind. Das System von zwei Flüssigkeitsschichten mit gleicher spezifischen Gewichte wurde dann folgendermassen hergestellt: Man nimmt je 300 bis 400 ccm. nicht mischbarer Flüssigkeit in einer Flasche mit geschliffenem Stöpsel, welche im Thermostat von 25°C. gestellt ist. Das dritte Komponent wurde dann in kleinen Portionen zugefügt, bis die spezifische Gewichte beider Schichten den gleichen Wert ergeben. Das spezifische Gewichte wurde, von Zeit zu Zeit, mit Ostwaldschem Pyknometer kontrolliert. Die Resultate sind auch in Tabelle 1 angegeben.

(3) Messung der Grenzflächenspannung und Viskosität. Weil das spezifische Gewicht beider Schichten gleich ist, die brauchbare Messanordnung wurde ziemlich beschränkt. Wir haben nach Bartell und Miller,[6] Kidokoro[7] usw. den Apparat in U-Form benutzt, wie in Abb. 1 skizziert ist. Die Grenzflächenspannung (σ) zwischen der Flüssigkeiten L_1/L_2 wird gegeben durch die Formel,

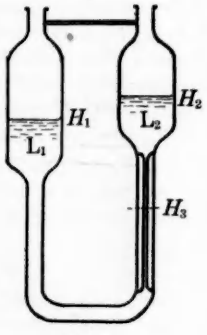


Abb. 1.

$$\sigma = \frac{gr}{2}(d_2h - d_1h'); \quad \begin{matrix} h = H_2 - H_3 \\ h' = H_1 - H_3 \end{matrix}$$

wobei,

r: Kapillarhalbmesser.
d_1, d_2: Spezifisches Gewicht von L_1 bzw. L_2.
H_1, H_2: Höhe der Oberfläche von L_1 bzw. L_2.
H_3: Höhe der Grenzfläche L_1/L_2.
g: Erdbeschleunigung,

bedeuten. Setzt man nach unserer Bedingung $d_1 = d_2 = d$, so wird die Formel einfach $\sigma = \frac{dgr}{2}(h - h')$. Aber die Messung selbst wird dadurch viel schwerer, denn die Flüssigkeitsgrenze H_3, unter dieser Bedingung, sehr leicht ausser der Kapillare verschoben wird, was die Messung unmöglich macht. Die Viskosität wurde gemessen an L_1 und L_2 separat mit Ostwaldschem Viskosimeter. Die erhaltene physikalische Konstanten sind in Tabelle 1 zusammengestellt. Nun könnte man mit diesen Systemen die Wirkung der Erdbeschleunigung und auch die chemische Reaktionen bei gewöhnlicher Temperatur ausschliessend annehmen. Weil deswegen Stabilisator bzw. Emulgator zu betrachtende Substanzen vollkommen nicht vorhanden sind, wird die Untersuchung der Emulgierungserscheinung ohne Nebenerscheinung damit ermöglicht werden.

(5) "International Critical Tables", IV, 436, New York (1928).
(6) Bartell und Miller, *J. Am. Chem. Soc.*, **50** (1928), 1961; **54** (1932), 936; **55** (1933), 2419.
(7) Kidokoro, dies Bulletin, **7** (1932), 280.

Tabelle 1.

	Komponent	Schicht-Zeichen	Spezifisches Gewicht (25°C.)	Viskosität	Grenzflächenspannung
A	Wasser Benzol Tetrachlorkohlenstoff	W.	0.9972	1.00	36.6
		NW.	0.9972	0.75	
B	Wasser Amylalkohol (iso) Chloroform	W.	0.9955	1.09	11.4
		NW.	0.9955	2.03	
C	Wasser Methylalkohol Benzol	W.	0.8701	1.29	3.6
		NW.	0.8699	2.76	

* W., NW.: Abkürzung von „wässeriger" und „nicht wässeriger" Schicht.

(4) Allgemeines über Vorgang des Emulgierens und Koagulierens. Wenn die chemisch wirkende Faktoren ganz ausgeschlossen sind, wie in unserem Fall, so ist leicht zu erwarten dass man dann die Grenzflächenspannung zuerst berücksichtigen muss. Wirklich das System C mit kleiner Grenzflächenspannung, lässt sich sehr leicht emulgieren durch schwaches Umrühren, wie z.B. durch nur einmaliges Umdrehen der Flasche. Wohingegen das System A, dessen Grenzflächenspannung am grössten ist, muss man mässig kräftig hin und her schütteln um zu emulgieren, unter dieselber Bedingung. Daraus ersieht man, dass die Emulgierung desto leichter vor sich geht je kleiner die Grenzflächenspannung ist. Trotz der Gleichheit der spezifischen Gewichte, sind die entstandene Emulsionen so unbeständig, dass sie schon in einigen Minuten nach dem Schütteln zu einem klaren zwei-flüssigen System, wie vorher, sich trennen. Da in diesem Fall die Trennung wegen der Verschiedenheit der spezifischen Gewichte zwischen disperser Phase und Dispersionsmittels praktisch vernachlässigbar ist, als die Ursache der Trennung, musste man die Koagulation durch Zusammenstoss der Tropfen in erster Linie in Betracht nehmen. Weil die Wahrscheinlichkeit des Zusammenstosses den Tröpfchenzahlen oder der Konzentration abhängig ist, haben wir die konzentrierte und verdünnte Emulsion separat behandelt. Die konzentrierte bedeutet die Emulsionen, welche aus annähernd gleichem Volum von Dispersionsmittel und disperser Phase entstanden sind, d.h. die Volumkonzentration 40 bis 60%. Die verdünnte versteht man die Volumkonzentration unter 10%. Selbstverständlich die Sache hängt ausserdem noch ab, von dem Emulsionstyp,[8] der Dispersität, der Homogenität der Tröpfchen usw., auf denen wir später wieder zurückkommen werden. Im fogenden wurden die Versuchsergebnisse nach 1–2 minutigen kräftigen Handschütteln beschrieben.

(a) *Konzentrierte Systeme.* Durch einfaches Handschütteln, lässt das System, in allen Fällen, zu einer ziemlich homogenen Emulsion dispergieren. Ihre Dispersität ist aber sehr grob. Die Tröpfchen sind,

(8) D.h. die Feststellung, welche Schicht des Systems (W. oder NW.) als disperse Phase in die andere dispergiert hat.

sofort nach dem Schütteln, schon einige zehntel mm. gross, welche mit blossen Augen leicht erkennbar sind. Die Vergrösserung der Tröpfchen durch Koagulation geht ziemlich schnell vor sich und nach 4–5 Minuten trennt sich die Emulsion zum klaren zwei-flüssigen System wie vorher. Trotzdem verläuft sich der Vorgang, wegen Gleichheit des spezifischen Gewichtes viel langsamer als anderer Fall, wie z.B. der Fall des Systems reines Wassers und Benzol usw., bei denen die Trennung schon in einigen Sekunden nach dem Schütteln erzogen wird, dass man kaum von dem Vorgang etwas beobachten kann. Wohingegen in unserem Fall, hat man doch genug Zeit den Koagulationsvorgang genau zu beobachten und einigen Schluss davon zu ziehen. Nun durch obenausgeführten Versuch wurde folgendes erkannt. Beim System B bzw. C mit kleinerer Grenzflächenspannung, wachsen die einzelne Tröpfchen langsamer zu, um dann die Flüssigkeitsmasse abzuspalten; während beim System A mit grösserer Grenzflächenspannung, die Tröpfchen sich schneller vergrössern und die Flüssigkeitsmasse scheidet sich auch viel früher aus. Der Vorgang wurde schematisch wie Abb. 2 bezeichnet. Dadurch überzeugt man sich darauf,

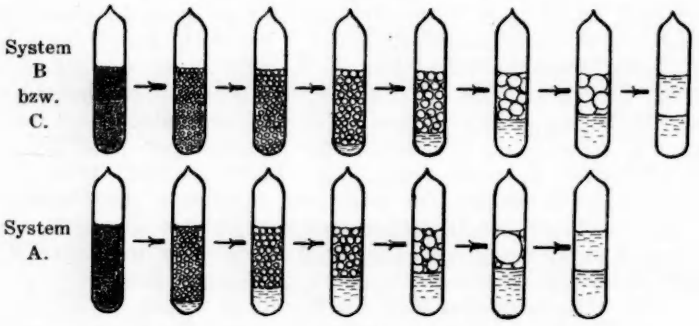


Abb. 2.

dass die Koagulation (oder der Rückgang der Emulgierung) wieder mit der Grenzflächenspannung abhängt, wenn sonstige chemisch wirkende Faktoren ausgeschlossen sind, wie in diesem Fall.

(b) *Verdünnte Systeme.* Verdünntes System lässt sich durch gewöhnliches Handschütteln kaum emulgieren. Wir haben die USW.[9] benutzt, um es zu emulgieren. Dazu schmilzt man 0.5 ccm. NW.-Flüssigkeit mit 4.5 ccm. W.-Flüssigkeit in einem Probiergläschen vom inneren Durchmesser 17 mm. zu und beschallt die USW. für eine Minute. Obwohl eine Schicht nur 10% beträgt, dispergiert sie niemals vollkommen in die anderen hinein, wie schon von Söllner und Bondy hingewiesen wurde.[10] Die W.-Schicht ergibt jedenfalls nach der Beschallung eine weiss trübe Emulsion ziemlich hoher Dispersität.[10] Der Zusammenhang von Beständigkeit der Emulsion mit Grenzflächenspannung und Viskosität des

(9) Abkürzung von Ultraschallwellen; siehe auch L. Bergmann, „Der Ultraschall", Berlin (1937); N. Sata und N. Naruse, *Kolloid-Z.*, **86** (1939), 102; N. Sata und Y. Niwase, *Kolloid-Z.*, **81** (1937), 294, usw.

(10) K. Söllner und C. Bondy, *Trans. Faraday Soc.*, **32** (1936), 616; **31** (1935), 835, 843.

Dispersionsmittels ist in Tabelle 2 ersichtlich. Also hier ist das System desto beständiger, je grösser die Grenzflächenspannung ist. Wie schon anfangs erwähnt, wenn man annimmt, dass die Grenzflächenspannung mit der Mischbarkeit (Löslichkeit) antibat zu betrachten ist, dann gibt es folgende Erklärungsmöglichkeit. Wir haben eben gesehen, dass durch USW. hergestellte Emulsion ziemlich fein dispers ist. Bekanntlich in einem dispersen System mässiger Dispersität findet die Löslichkeitserhöhung disperser Phase statt, durch dessen Folge die Vergrösserung gröberer dispersen Teilchen auf Kosten feinerer dispersen Teilchen

Tabelle 2.

System	A	B	C
Komponent	Wasser Benzol Tetrachlorkohlenstoff	Wasser Amylalkohol (iso) Chloroform	Wasser Methylalkohol Benzol
Grenzflächenspannung	36.6	11.4	3.65
Viskosität von W-Schicht	1.00	1.09	1.29
Beständigkeit	Nach 4 Tagen, noch Spur trübe	Nach 1 Tage, ganz klar	Nach 4–5 Stunden, schon ganz klar

geschehen wird.[11] Dann solche Erscheinung selbstverständlich leichter im System C als im System A zu geschehen ist, welche die Unbeständigkeit der Emulsion verursachen könnte; denn die gegenseitige Löslichkeit beider flüssigen Schichten vom System C grösser als vom System A ist. Hier kann man aber nicht einfach bestimmtes sagen, weil unter 10%-Emulsion eines Flüssigkeitspaares zwei Sorten der Emulsionstypen, namentlich NW/W- und W/NW-Typ zu verstehen sind. Der Versuch muss unter besonderer Rücksicht des Emulsionstyps ausgeführt werden. Wenn man daran denkt, dass die Viskosität des Dispersionsmittels die Bewegung der dispersen Teilchen verhindern kann, ist die Parallelität zwischen Viskosität des Dispersionsmittels und Beständigkeit leicht zu verstehen.

(Fortsetzung folgt.)

(11) H. Freundlich, „Kapillarchemie", I, 218, Leipzig (1930).